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SPE TRANSACTIONS

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AN EMPIRICAL METHOD FOR THE PREDICTION OF LIQUID PERMEATION IN POLYETHYLENE AND RELATED POLYMERS

Morris Salame
Plax Corp., Hartford, Conn.

Permeability properties depend on the size, shape and polarity of the permeating molecule. Permeability of organic liquids, polar or non-polar, can be quite accurately predicted if the chemical composition of the permeant is known. By the choice of an arbitrary value (unity) as an indicator for the carbon atom, numbers specific to each structural element of the permeating molecule can be computed from previous experimental data. These numbers, herein called "Permachor" values (π), then combine by simple addition to relate the logarithm of a liquid's permeation in polyethylene.

THE THERMODYNAMICS OF BIAXIAL ELONGATION

Richard S. Stein
Department of Chemistry, University of Amherst, Amherst, Massachusetts

If temperature variations of forces in both directions are observed simultaneously at constant simple dimensions, internal energy and entropy changes on elongation in those directions may be calculated at constant volume and in the more common experimental condition of constant pressure. Thermodynamic derivatives at constant volume are important for fundamental molecular interpretation being related to configuration change. Constant pressure quantities were therefore changed into constant volume ones by the use of an evaluated correction term, involving average Young Moduli and thermal expansion coefficient.

POLYMERS AS CONDUCTORS AND SEMI-CONDUCTORS

M. Becher, S. M. Atlas and H. F. Mark
Bronx Community College, Bronx, New York

Mobile ions can be introduced thereby increasing the conductivity, with a limiting operating temperature range of 200°-250°C. Conductivity can be increased with the formation of conjugatd double bonds. Polymeric compounds may be synthesized with metallocyclic groups, where an atom of metal is bound to nitrogen atoms in a heterocyclic system in the basic chain of conjugation of the macromolecule. Here phtalocyanimes possess the greatest thermal stability. Lastly there are semiconducting polymers with conjugated double bonds containing hetero-atoms in the principle chain, having unpaired electrons of oxygen and nitrogen.

DYNAMIC MEASUREMENT OF MECHANICAL MODULI I

Armand F. Lewis and Marvin C. Tobin
American Cyanamid Co., Central Research Division, Stamford, Conn.

Equipment is described for measurement of Young's and shear modulus on the same identical polymer sample, by a free-vibration method. Strain gauges are used as sensors in an automatic recorder. Young's modulus and damping, shear modulus and damping and Poisson's ratio are reported over a range of temperature for polypropylene, Nylon 66 and poly(methylmethacrylate). It is found that Poisson's ratio shows a dip in the glass transition region and that values greater than the infinitesimal strain limit of 0.5 are obtained in the rubbery region.

PHYSICAL TECHNIQUES USED IN STUDYING INTERFACIAL PHENOMENA

R. L. Patrick
Alpha R & D, Inc., Blue Island, Illinois

Adsorption studies on powdered and planar surfaces yield significant information regarding the rate and degree of interaction between the substrate and the organic adsorbate. Investigative tools include contact angle measurement, radiotracer methods, ellipsometry, x-ray diffraction, electron diffraction, elegant infrared techniques, dynamic desorption techniques, and film balance applications.

clip these briefs for easy reference on 3" x 5" or other suitable filing cards

INTERACTION OF ORGANIC MONOMERS AND WATER WITH FIBERGLASS

K. Gutfreund and H. S. Weber
Armour Research Foundation of Illinois Institute of Technology, Chicago 16, Illinois

Interfacial reactions between organosilane-treated fiberglass and styrene, and bond conditions in these and in polymerized ethylene oxide and epichlorhydrin-E-glass systems were investigated. The vinyl functionality of some alkenylsilanes showed little effect on the polymerization of styrene on E-glass. The polymerization of this aromatic monomer on vinyltrichlorosilane-reacted fiberglass did not result in interfacial bond formation. Sorption of water on organosilane-coated glass at different temperatures suggested that permeation of the adsorbate into the bulk of the substrate was determined by diffusive transfer of water molecules.

CHEMISTRY OF CHROMIUM COMPLEXES USED AS COUPLING AGENTS IN FIBERGLASS RESIN LAMINATES

Paul C. Yates and John W. Trebilcock
E. I. du Pont de Nemours & Co., Inc., Wilmington, Delaware

The chromium complex is chemically bonded by ion exchange with alkali cations to strongly acidic sites in the glass surface. These sites are formed by the isomorphous replacement of silicon by boron and aluminum in the network structure. Polymerized complexes are better bonding agents than monomeric ones. Specific interactions between organic groups on the chrome complex and the bonding resins also determine laminate strength and water resistance.

A STUDY OF THE FINISH MECHANISM: GLASS TO FINISH, FINISH THICKNESS AND FINISH TO RESIN

William J. Eakins
DeBell & Richardson, Inc., Hazardville, Connecticut

A solution of substituted alkyl alkoxy silanes was applied to E-glass filament strands before forming glass-resin composite hoops, which were tested to relate changes in hoop physical properties to the nature of the coupling agent-size application. Continuously heat cleaning E-glass in oxygen-enriched air gives a strand that, when properly coated with size and laminated, makes a hoop with superior strength and modulus properties.

A NEW INTERPRETATION OF THE GLASS-COUPLING AGENT SURFACE THROUGH USE OF ELECTRON MICROSCOPY

S. Sterman and H. B. Bradley
Union Carbide Corp., Tonawanda, N. Y.

Theoretically a monolayer or insignificant weight per cent of coupling agent should give optimum properties for fiber glass-resin composites, contrary to commercial practice. Studies of variation of chemical bonding between the coupling agent and the resin and the study of the degree of bonding of the coupling agents to the glass by extraction techniques have not explained this effect. However, new techniques of electron microscopy have revealed details of loading distribution and agglomeration on the glass fiber which tend to explain this effect.

THE DEGREE OF BONDING BETWEEN COUPLING AGENTS AND GLASS FILAMENTS

William J. Eakins
DeBell and Richardson, Inc., Hazardville, Connecticut

Evidence indicates that there is a chemical bond between the coupling agent of either silane or chrome complex type and the glass substrate, but that this chemical bond may be strong or weak, depending on the elements making up the bond and the other elements in the immediate area surrounding the bond. These elements can exert either a beneficial or detrimental effect on the strength of that bond. Other evidence is given to show that a vapor phase treatment that applies silane coupling agents like A-1100 to "E" glass gives the highest known strength retention values. A mechanism is advanced to explain the bridging of unreactive sites on glass surfaces by silane coupling agents applied from solution.

First Year for

SPE TRANSACTIONS

This is the fourth issue of SPE TRANSACTIONS for 1961. The enthusiasm with which this publication has been received is evidence of its service to polymer chemists and plastics engineers interested in new developments in polymer science and technology. The 1100 subscribers who are engaged in work in this field attest to the need for this new fundamental journal.

It is with gratitude that we cite the confidence of the many contributing authors who are submitting manuscripts for publication. Because of the quality of these papers and the work that they represent, TRANSACTIONS has achieved impressive stature in less than one year.

An ever accumulating body of knowledge gathered by experienced scientists in an expanding field will be the basis of future articles. Such literature will become increasingly more important as factors contributing to the future development of the plastics industry.

This issue of TRANSACTIONS contains more technical articles than those you have received heretofore, reflecting the additional number of worthwhile contributions received. This expansion is a part of a master plan which will eventually result in more and longer issues of TRANSACTIONS. As always, manuscripts are carefully selected and reviewed before publication by an authoritative and exacting Editorial Advisory Board.

In keeping with the policies of the Society of Plastics Engineers, more significant, educational and informative articles on polymeric materials are being planned for our second volume, beginning January, 1962.

An Empirical Method For . . .

The Prediction Of Liquid Permeation In Polyethylene And Related Polymers

Morris Salame

Plax Corp., Hartford, Conn.

Permeability of organic liquids can be accurately predicted if the chemical composition of the permeant is known. Size, shape, polarity and interaction forces are taken into account in determining this quantity

With the advent of polyethylene there came the increasing demand to package both pure chemicals and proprietary products in polyethylene film and containers. Polyethylene has a high degree of inertness to practically all chemicals but, being a plastic, it is permeable. The degree of permeability sometimes becomes a limiting use factor. Early literature revealed little more than gas permeation data and the water vapor transmission of the polymer. It was in 1947 that Plax began its permeability studies to obtain the information needed to determine which liquids could be safely packaged in polyethylene.

Permeability Studies

Initial experimentation consisted of heat sealing various test fluids in polyethylene bags made from lay-flat TM tubing. The bags had a known surface area and wall thickness and from their observed weight losses over a period of time permeability factors (P-f) measured in gm./24 hr./100 in.^{2}/mil were calculated. (1)

The effects of the polarity and the size of the permeating molecule were noted. Parliman used the expression $(e - n^2)$ as a measure of the polarity of the permeant (e and n being the dielectric constant and the refractive index of the liquid respectively) and the normal boiling point of the liquid to indicate the size of the molecule. These he combined into the expression $(e - n^2)T^2$ which he correlated to P-f. The correlation was effective for compounds containing carbon, hydrogen and oxygen but those containing nitrogen were most erratic. An empirical formula for the prediction of P-f was not derived but such an expression was indicated.

Permeability study was continued using 4 oz. capacity Boston Round bottles (instead of bags) having wall thicknesses of 30-40 mils. Many of the tests were continued for 365 days at temperatures ranging from 32°F-165°F. The accumulated data and evaluation appear in W.A.D.C. TR 53-133 parts 1-42 (2).

Bent, (3) after analyzing this data, expressed the relationship of permeability to temperature as:

$$P = P_o \, e^{-E_p/RT} \qquad (1)$$

where P is permeability factor

P_o is a constant
E_p is Apparent Energy of Permeation
R is the Universal Gas Constant
T is absolute temperature

From the permeability data at various temperatures plots of the logarithms of P (permeability) against the reciprocal of absolute temperature were obtained. The plot of each individual permeant proved to be a straight line with a slope related to E_p. This value might well be considered the apparent energy of permeation of the molecule in the polymer. By extrapolating the line to $1/T = 0$ the value of P_o could also be found. It was thus that the E_p and P_o parameters were determined.

In order to determine the E_p for a given permeant it was necessary to measure its permeability at several temperatures. It was later found that the E_p parameter could be determined from the empirical formula:

$$E_p = 0.0348 \; V + 0.75 \; V/L + 2.4 \; \Delta\Delta H \qquad (2)$$

V (molecular volume) and L (molecular length) were determined from measurements of Fisher-Hirschfeld models. A constant related to the heat of vaporization of the permeant $\Delta\Delta H$ was chosen as a measure of polarity. The rates of permeation not only vary with temperature but vary with the size, shape and polarity

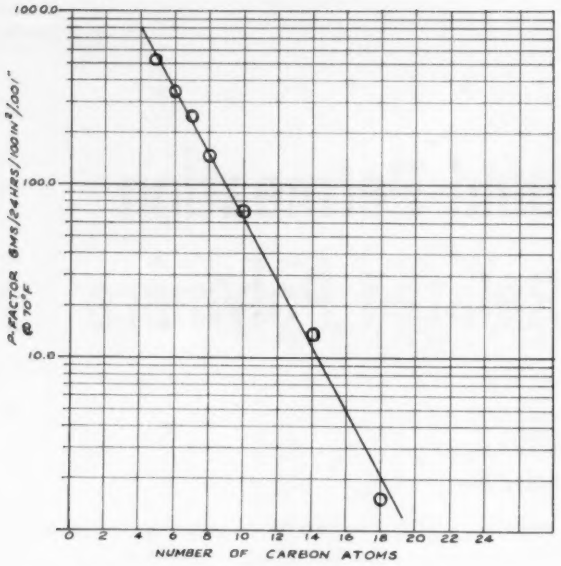

Figure 1. Permeability of straight-chain hydrocarbons vs number of carbon atoms in chain (70°F)

of the permeant. These factors have been expressed in the above terms to measure the energy of permeation E_p.

E_p may be determined in this way but at least one permeability test must be made to obtain a permeability in order to calculate P_o. While it was still not possible to calculate permeability of an untested permeant from hand-book values its permeability at any or several temperatures may be closely estimated from a single test.

Derivation of the Permachor Method

The rate at which a given molecule permeates through polyethylene has been shown to be dependent upon various properties of the permeant such as size, shape, polarity and other factors. Any attempt to correlate P-factors with a single property of the permeant such as size alone gives rise to a wide scatter of points. It was observed, however, that for the non-polar homologous series of straight-chain hydrocarbons a plot of P-factors versus the number of carbon atoms in the permeant did indeed yield a straight line relationship on semi-log paper. This is shown in *Figure 1*. Working from this curve, numerical values were empirically assigned to other atoms and organic radicals so as to force the permeability points of other homologous series to fall on the same straight line. As an example, the unsaturated hydrocarbons were examined and their P-factors when plotted similarly to *Figure 1* formed a straight line which was shifted by a factor of 0.2 to the right of the saturated compounds' line. Thus, by assigning a value of minus 0.2 to the double bond the P-factors of the unsaturates fell in line with the saturates. The permeability data of the balance of varying types of organic liquids, polar as well as non-polar, were examined and values assigned to them by merely noting the distance they were shifted from the original line when plotted against the number of C atoms in each molecule. In doing this, the number of C atoms in the compound being studied was first totalled and the difference between this

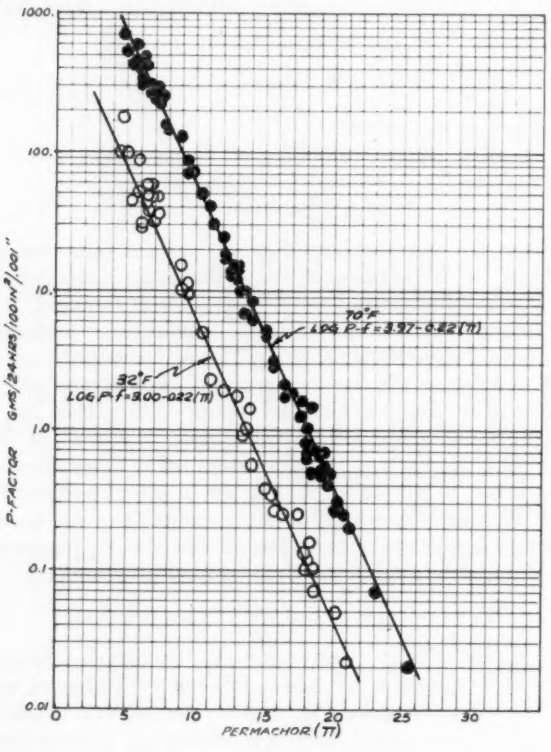

Figure 2. Permeability vs permachor π for low-density polyethylene @ 32°F (0) and 70°F (0)

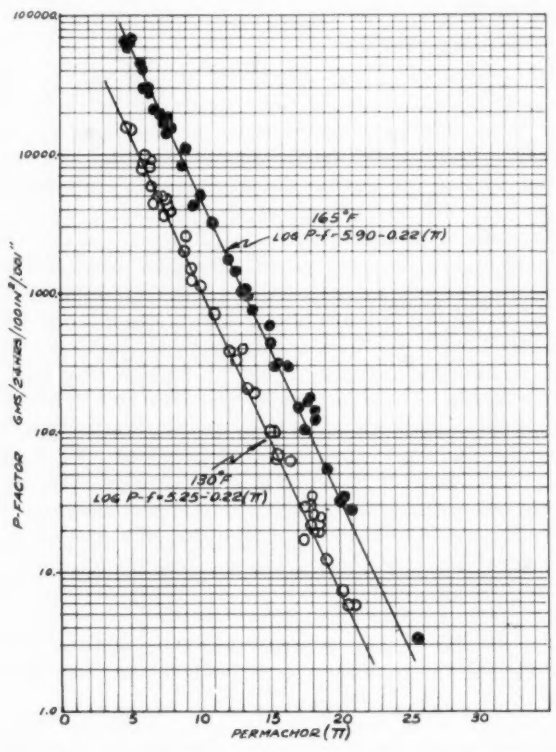

Figure 2a. Permeability vs permachor for low-density polyethylene @ 130°F (0) and 165°F (0)

Table 1. Permachor π Values to be Used in Estimating P-Factors by Equation 1

Atom or Group	NUMBER OF CARBON ATOMS IN MOLECULE										
	1	2	3	4	5	6	7	8	9	10	>10
	Permachor (π) Value for Atom or Group										
Carbon (—C—)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	0.93
Chlorine (—Cl)	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2	1.2
Bromine (—Br)	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
Sulfur (—S)	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0	4.0
Nitrate (—NO_3)	15.4	13.4	13.4	13.4	13.4	9.6	9.6	9.6	9.6	9.6	9.6
Ether (—O—)	—	2.4	2.4	2.4	2.4	1.4	1.4	1.4	1.4	1.4	1.4
Ester ( )	—	9.6	9.6	8.0	7.0	7.0	7.0	3.1	3.1	3.1	3.1
Ketone ( )	—	10.8	10.8	8.5	8.5	8.5	8.5	8.5	8.5	8.5	8.5
Aldehyde ( )	17.8	12.0	12.0	9.5	9.5	8.0	8.0	8.0	8.0	8.0	8.0
Anhydride ( )	—	15.8	15.8	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0
Amide ( )	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0	18.0
Amine (—NH_2) Aliphatic	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0	6.0
Amine (—NH_2) Aromatic	—	—	—	—	—	11.0	11.0	11.0	11.0	11.0	11.0
Alcohol (—OH) Aliphatic	16.5	16.5	15.5	14.0	14.0	11.0	11.0	10.0	10.0	10.0	10.0
Alcohol (—OH) Aromatic	—	—	—	—	—	13.0	13.0	13.0	13.0	13.0	13.0
Acid ( ) Aliphatic	18.0	13.5	13.5	11.0	11.0	11.0	11.0	11.0	11.0	11.0	11.0
Acid () Aromatic	—	—	—	—	—	14.0	14.0	14.0	14.0	14.0	14.0
Phenyl ( ) Benzene	—	—	—	—	—	5.4 below 80°, 7.6 above 80°F					
Mono, ortho & meta	—	—	—	—	—	5.4	5.4	5.4	5.4	5.4	5.4
Para	—	—	—	—	—	3.8 below 80°, 5.4 above 80°F					
Alicyclic ( )	Add 1.0 below 80°, 2.0 above 80°F										
Iso subst. & Side Brnch'g	Add 2.0										
Double Bond Between Carbons	Substract 0.2										

figure (using unity as the value for C) and the value which was required to place the point on the basic line was then the number assigned to the particular type of molecule under consideration i.e. an alcohol, an ester, an aldehyde, an acid, etc. These numbers have been listed in *Table 1* and are called the Permachor (π) values of the molecule; the numbers are simply additive when calculating the Permachor of a particular compound.

Once the tabulation of Permachor values was completed it was noted that the same Permachor which had been derived from data at 70°F could be used at any temperature and still yield a straight line relationship between P-factor and Permachor. Furthermore, the slope of the lines is the same at any temperature: 0.22. This can be seen in the Master *Figures 2 and 2a* where the P-factors of over 70 organic liquids are plotted against Permachor values assigned as described above. The simple equation that fits these lines is:

$$\log \text{P-f} = \text{K} - 0.22\pi \qquad (3)$$

where: P-f is the permeability factor of the liquid expressed in (grams/24 hrs/100 in²/0.001 in.)
K is a constant related to temperature alone and
π is the Permachor value.

Further investigation showed that the K constant of Equation 3, which is merely the intercept of the lines with the absissca, could be related to temperature by the equation:

$$K = 16.55 - 3700/T \qquad (4)$$

with T in degrees Kelvin.
For example, K is 3.00 at 32°F, 3.97 at 70°F, 5.25 at 130°F and 5.90 at 165°F. A more complete listing of K values appears in *Table 5*.

Table 2. Effect of Carbon Backbone Length on Polarity

Compound	Permachor of Hydroxyl alone (From Table 1)	e (Dielectric Constant)
C_1-OH	16.5	33.6
C_2-OH	16.5	25.1
C_3-OH	15.5	22.2
C_4-OH	14.0	17.8
C_5-OH	14.0	14.8
Phenyl-OH	13.0	10.6
C_8-OH	10.0	10.3

Table 3. P-Factors for Polyethylene

Permeant	Permachor		P-factor 32°F	(grams/24 hrs/100 in²/0.001 in) 70°F	130°F	165°F
n-Propanol	18.5	Cal'd	0.07	0.8	15	66
		Exp'l	0.07	0.5	22	168
Acetone	13.8	Cal'd	0.9	8.5	160	720
		Exp'l	1.4	6.8	184	750
n-Hexane	6.0	Cal'd	48.0	450.0	8500	38000
		Exp'l	48.0	350.0	9000	30000
p-Xylene	5.8 & 7.4	Cal'd	54.0	500.0	4100	19000
		Exp'l	85.7	486.0	4800	16300

Table 4. Experimental and Predicted P-factors of 11 Organic Liquids Used to Test Permachor Method

Permeant	Permachor Value (π) (From Table 1)	Predicted P-factor (From Eq. 1)	Experimental P-factor
1,1,1-Trichloroethane (Vythene)	5.6	550	260
Methyl cyclohexane	7.0	270	275
o-Dichloromethane	7.8	180	155
1,2-Dibromomethane	8.0	160	140
Nitromethane	16.4	2.3	2.1
m-Chloroaniline	17.6	1.3	1.6
Diethyl oxalate	18.4	0.6	0.7
Benzyl alcohol	19.4	0.5	0.4
2-Ethyl hexanol	20.0	0.36	0.30
Furfuryl alcohol	20.6	0.27	0.24
Chloromaleic anhydride	23.0	0.08	0.07

The relationship of the Permachor to the size, shape and polarity of each particular atom or radical can readily be seen in *Table 1*. The Permachor increases as the group either increases in size, becomes bulkier or becomes more polar. For the simple hydrocarbons the increase in Permachor is just the increase in the number of carbons in the chain. For the unsaturates the Permachors are the same except they are reduced by a factor of 0.2 for each double bond (indicating the shortening of the chain). In this manner one can compare the Permachors from one group to the next and although they were assigned on a purely empirical basis (using actual permeability data) the theoretical basis for the differences in their magnitudes can be readily seen.

There are certain shape factors which also become evident in the Permachors. The iso-substitution in a molecule, as well as side branching, increases the bulkiness of the molecule and so reduces its permeability over and above the reduction caused by size alone. For this reason a value of 2.0 is assigned to any iso or branched group in calculating the Permachor of the molecule. This value was found by noting that the P-factors of branched molecules were all shifted by a factor of 2.0 from the basic curve. Permachors of other shape factors were calculated similarly.

In the case of polar groups and radicals polarity greatly increases the Permachor value. For most polar liquids polarity is the controlling factor in its rate of permeation and size and shape are of less importance. In comparing the Permachors within any one polar group, for example the hydroxyl (—OH), it will be noticed that its Permachor value decreases as the molecule in which it is present increases in the number of C atoms in the backbone. This reduction in Permachor value for the hydroxyl, as well as for other polar groups, indicates a reduction in polarity. This is due to the fact that as the non-polar carbon backbone of the molecule increases in size the polar charge of the polar group becomes less dominant so far as permeability is concerned. This can be shown by comparing the dielectric constants, which are indicators of polarity, of the alcohols. This is shown in *Table 2*.

This decreasing effect is also seen with the nitrates, the acids, the ethers, the esters, the ketones and the aldehydes. The Permachors for certain polar groups when in an aromatic compound are higher than they would be when in an aliphatic of the same number of C atoms. This is due to the high resonance energy of the phenyl when in association with a polar grouping. This can be seen with the aromatic amines ($\pi = 11$), aromatic hydroxyl ($\pi = 13.0$) and aromatic acid ($\pi = 14.0$).

Use of Permachor Method

As examples of the use of the above method four liquid permeants have been chosen—an alcohol, a ketone, a straight chain and an aromatic hydrocarbon. The following calculations indicate the way in which Permachor values are found for compounds from *Table 1*. Calculations of the Permachor values for example permeants:

n-Propyl alcohol	C_3H_7OH	3(C) @ 1.0 each = 3.0 1(OH) @ 15.5 = 15.5	
		Total π = 18.5	
Acetone	CH_3COCH_3	3(C) @ 1.0 each = 3.0 1(=O) @ 10.8 = 10.8	
		Total π = 13.8	
n-Hexane	C_6H_{14}	6(C) @ 1.0 each = 6.0	
		Total π = 6.0	
p-Xylene	CH_3 ⬡ CH_3	2(C) @ 1.0 each = 2.0 1(p-phenyl)* = 3.8	= 2.0 = 5.4
		Total π = 5.8	& = 7.4

Now that the Permachors have been calculated for the above examples their P-factors in polyethylene at any temperature may be estimated using Equations 3 and 4. This has been done in *Table 3* at 32°, 70°, 130° and 165°F.

Also listed in the table are the actual P-factors from experimental bottles tests for comparison:

As is indicated in *Table 3*, agreement is very good with actual P-factors experimentally calculated from bottle loss data. (It must be emphasized that actual P-factor tests when made on a bottle of changing volume, variations in wall thickness, slight variations in temperature, etc., are only accurate in themselves within a certain plus and minus range. Furthermore, variation is more likely than when the data is based on film tests.) The average error in the 16 determinations illustrated above is only 20%. The largest errors appear in the alcohol (60%) which is highly polar. In general, however, the method is only slightly less accurate for polar materials. Although only four examples have been shown the Permachor method has been shown applicable to most organic liquids which contain radicals, atoms or groups which appear in *Table 1*. For groups and molecules containing atoms and radicals which do not appear in *Table 1* only one permeability test at any one temperature is required in order to calculate the Permachor for the missing atom, group or radical. This automatically enables one to predict the P-factor of any other molecule containing that particular element. Permachor values may however be estimated from known size, shape and polarity data.

Validity of Permachor Method

To test the validity and usefulness of the system, organic liquids for which P-factors had never been experimentally determined were tested at 73°F in 4-oz. polyethylene bottles and their P-factors calculated. P-factors were also estimated using Equation 3 and the Permachor values from *Table 1*. The results are shown in *Table 4*.

Agreement is excellent for 10 of the 11 tested. The only exception is Vythene which gave a much lower value than predicted. This could be due to the fact that the liquid contains an unspecified inhibitor. (If the inhibitor is present in a relatively large amount and is a molecule with a high Permachor value, the lower P-factor found can be explained.) For the balance of the test liquids prediction is at the most 25% in error and the average error is under 14%. Thus the accuracy of the Permachor is shown.

Appendix 1 lists more than 70 organic liquids whose permeability factors in polyethylene have been experimentally determined in the Plax laboratories. The table lists the compounds in their respective classes along with the Permachor values calculated from *Table 1*. The permeation rates at four temperatures determined by actual tests and those calculated using Permachor values and Equations 3 and 4 are also listed for comparison. This is the data which has been plotted in the Master *Figures 2 and 2a*.

An examination of the permeation values shows remarkable agreement between calculated and experimental values. When making these comparisons, note that the experimental values have been obtained from bottle tests, film-cup tests and extrapolations of test data obtained at other temperatures. Using the Permachor values it is not possible in all cases to calculate the exact permeability of polyethylene to an untested permeant but an accurate estimate approaching an actual value is possible as was shown in *Table 4*.

In general the method is more reliable at the lower temperatures. This is due to the fact that at high temperatures the molecules of both polyethylene and the permeant are in more excited states of motion and tend

Table 5. Values of K at Various Temperatures From Equation 2 (Values are for regular polyethylene unless otherwise indicated)

T (°F)	K
0°	2.05
32°	3.00
40°	3.20
50°	3.50
60°	3.75
70°	3.97
73°	4.05 (3.21*) (3.36**) (4.17***)
80°	4.20
90°	4.40
100°	4.65
110°	4.85
120°	5.05 (4.10****) (4.98***)
130°	5.25
140°	5.45
150°	5.60
160°	5.80
165°	5.90
170°	5.95
180°	6.15
190°	6.30

* For Ziegler-type high-density polyethylene
** For Phillips-type high-density polyethylene
*** For polypropylene using 0.26 π
**** For all high-density polyethylenes
A plot of K values versus temperature for regular polyethylene appears in Figure 3.

* The Permachor value of the para-phenyl is lower at 32°F and 70°F due to its "streamlined" structure. At high temperatures (i.e. above 80°F) the value reverts to its true value of 5.4 (6 carbons and 3 double bonds) since shape factors become less dominant due to increased molecular motion. Thus the Permachor of p-xylene below 80° is 5.8 and above 80° is 7.4.

to give more unpredictable permeability results due to changing shape and polarity factors. Furthermore, melting-out of the crystallites in the polymer at the higher temperatures produces a more amorphous system thereby increasing permeability over and above predicted values. (The crystallites act as barriers to permeation since only the amorphous areas are permeable.) When comparing predicted P-factors at higher temperatures with experimental data, however, it should be kept in mind that although the predicted factor may be off by as much as 1000, the actual percent error will be low.

Effect of Temperature

The fact that the same Permachor can be used at any temperature is due to the fact that most organic liquids have log P-f vs 1/T slopes of about the same magnitude (within a narrow range). Thus all liquids have the same log P-f vs Permachor slope (0.22) and this proves to be of great advantage in the method. The only difference in the various temperature lines lies in the intercept with the P-f axis as is seen in the Master Figures. This intercept is the K value of Equation 1 and is simply related to temperature by:

$$K = 16.55 - 3700/T \qquad (4)$$

with T expressed in Absolute Temperature (Kelvin)

With this expression the K value at any temperature may be found to be used in Equation 1. As an example the P-factor of a liquid will be calculated at 95°F. Assume the permeant is n-Hexane which has a Permachor of 6.0 (6 carbons @ 1.0 each). To find K:

$$95°F = 35°C = 308°K$$
$$K = 16.55 - 3700/308 = 4.55$$

Next, using Equation 3:

$$\log \text{P-f} = K - 0.22\pi \qquad (3)$$
$$\log \text{P-f} = 4.55 - 0.22(6.0) = 3.21$$

or

$$\text{P-f} = 1600 \text{ (gms/24 hrs/100 in}^2\text{/0.001 in)}$$

For convenience the K values at various temperatures ranging from 32°F to 190°F have been calculated and listed in *Table 5*. *K* values for other polymers which are discussed in a later section are also listed.

The fundamental relationship between liquid permeability in polyethylene and temperature is the Arrhenius-type equation:

$$\text{P-f}^{\circ} = P_o e^{-E_p/RT} \qquad (1)$$

as Bent (3) pointed out. In order to predict permeability of a particular permeant at a particular temperature both E_p and P_o must be known. Bent empirically related E_p to various size and polarity parameters of the permeant Equation 2 but in order to calculate P_o at least one permeability test of the liquid must be made as was pointed out earlier. By the use of the Permachor method, however, all that need be known of the permeant is its Permachor (π) from *Table 1*. By the following treatment of the Permachor equation it will be shown that it is analogous to Equation 1:

° P or P-f represent the permeability factor.

Step 1: $\log \text{P-f} = K - 0.22\pi$ (3)
substituting in the value of K:

Step 2: $\log \text{P-f} = 16.55 - 3700/T - 0.22\pi$ (combine 3 and 4)
converting to Natural logarithms (multiply by 2.3):

Step 3: $\ln \text{P-f} = 38.10 - 8500/T - 0.50\pi$
inserting R (1.987) into the last two terms:

Step 4: $\ln \text{P-f} = 38.10 - 16900/RT - \pi T/RT$
which is equivalent to:

$$\text{P-f} = (3.55 \times 10^{16})\, e^{\frac{-16900 + \pi T}{RT}} \qquad (5)$$

When one compares Equation 5 with Equation 3 it will be noticed that by using the Permachor method P_o is no longer a variable from one liquid to the next, but is a constant for any and all liquids (3.55×10^{16}). The remaining parameter, E_p, then becomes a function of the Permachor alone and temperature. A knowledge of the Permachor alone allows the P-factor to be predicted at any temperature.

Permeability of Other Polymers

Using the meager data available of the liquid permeability of other polymers it was seen that the same Permachor values derived for regular polyethylene can be used to predict P-factors in related polymers. These other polymers include high-density polyethylene as well as polypropylene—which are both non-polar. The method is not applicable, however, to polar polymers such as nylon, Delrin, Penton and other nitrogen or oxy-

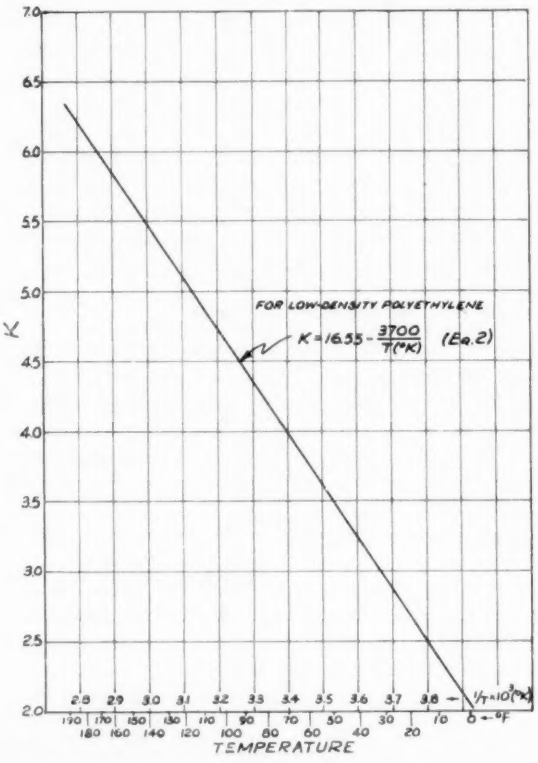

Figure 3. K of Equation (3) vs Temperature

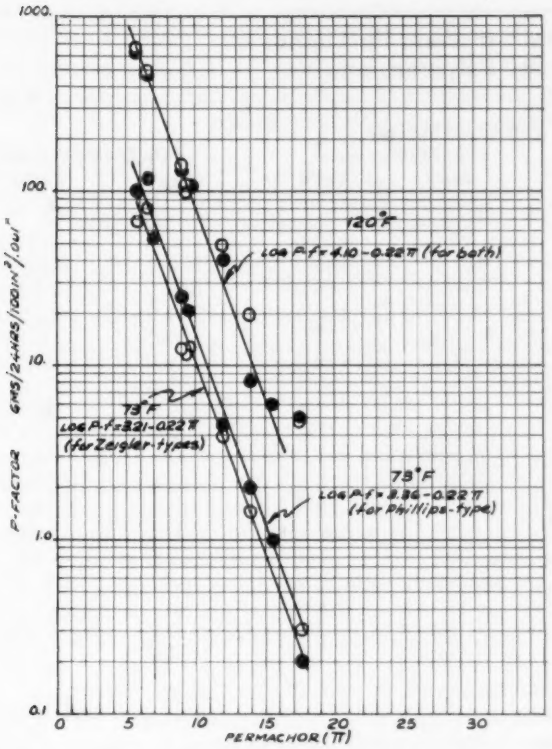

Figure 4. Permeability vs permachor π tor high-density polyethylenes Ziegler—types (0) Phillips—type (0) @ 73°F and 120°F

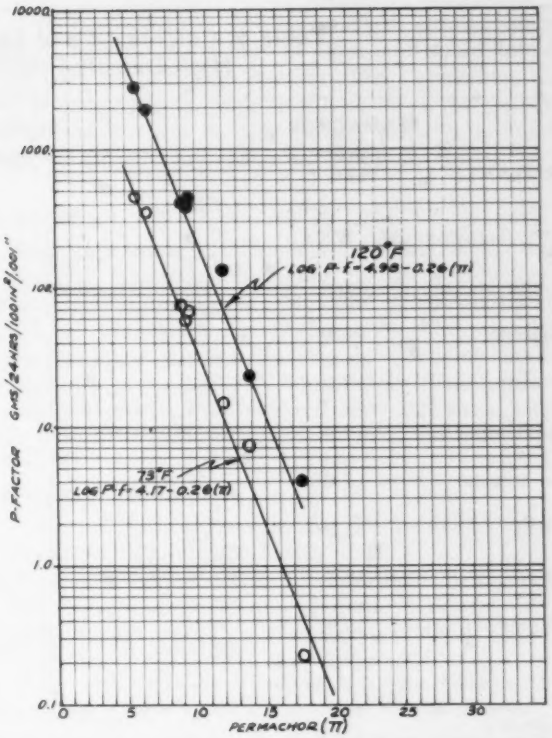

Figure 5. Permeability vs permachor for polypropylene @ 73°F (0) and 120°F (0)

gen-containing plastics. This is due to the fact that the Permachors for the permeants are calculated assuming a non-polar polymer as the substrate.

Naturally, the constants in the Permachor equation will not be the same for other polymers but a straight-line relationship does exist for Permachor (π) versus P-factor for all hydrocarbon polymers. The data available for the high-density polyethylenes has been assembled in *Figure 4* and for polypropylene in *Figure 5* using the same Permachor already listed in *Table 1*. *Table 6* lists the experimental permeability data as well as the predicted values for comparison.

A. High-Density Polyethylenes—The same equation (1) used to predict P-factors in regular polyethylene may be used here except that new K factors must be employed. The equation which relates K to temperature for regular polyethylene (Eq. 4) may not be used for the high-density polymers. The K factors to be used with Equation 3 are:

$$K = 3.21 \text{ for Ziegler-type @ } 73°F$$
$$K = 3.36 \text{ for Phillips-type @ } 73°F \text{ and}$$
$$K = 4.10 \text{ for any type @ } 120°F$$

Sufficient data at other temperatures does not exist to relate K to temperature as was done for the regular polymer.

As can be seen from the Table and Figure the Phillips-type polymers have higher liquid permeability than the Ziegler-types. Since both polymers are linear and contain about the same percent crystallinity one must conclude that the crystallite morphology is different in the two polymers. Michaels and Bixler (4) found this to be true also for the gas permeability of the polymers and came to the conclusion that the crystallites in the Ziegler polymers are more anisometric, creating a better barrier to diffusion. At 120°F, however, the P-factors for the two plastics approach each other. This may indicate that crystalline melt-out is more rapid in the Ziegler type.

B. Polypropylene—It will be noticed that liquid permeability is higher in polypropylene than in high-density polyethylene and in some cases even regular polyethylene. Since the crystallinity in polypropylene is very high one would expect permeability to be low since permeability can take place only in the amorphous areas. Since permeability is high, however, it leads to the conclusion that the intermolecular distances between chains or crystallites in polypropylene must be much greater than those of polyethylene. This is borne out in the lower density of the polymer.

Equation 3 which is used for the polyethylenes cannot be used for polypropylene due to the fact that the slope of the correlation is no longer 0.22. The polypropylene equation is:

$$\log \text{P-f} = K - 0.26\pi \qquad (6)$$

where

$$K = 4.17 \text{ @ } 73°F \text{ and}$$
$$K = 4.98 \text{ @ } 120°F$$

Again the same Permachors of *Table 1* can be used for this polymer.

Table 6. Calculated and Experimental P-Factors for Liquids in High-Density Polyethylenes and Polypropylene

PERMEANT	PERMACHOR π (from Table 1)		HIGH-DENSITY POLYETHYLENES 1. Ziegler-type Exp'l	Cal'd*	2. Phillips-type Exp'l	Cal'd*	POLYPROPYLENE Exp'l	Cal'd**
Carbon Tetrachloride	5.8	73°F	68.0	85.0	98.0	120.0	460.0	456.0
		120°F	670.0	660.0	637.0	660.0	2800.0	2960.0
Toluene	6.4	73°F	80.0	63.0	118.0	89.0	360.0	323.0
		120°F	500.0	490.0	496.0	490.0	1954.0	2090.0
Dipentene	8.9	73°F	13.0	17.8	25.6	25.0	75.0	72.5
		120°F	139.0	138.0	136.0	138.0	409.0	468.0
n-Decane	9.3	73°F	11.4	14.5	—	20.4	57.0	56.2
		120°F	98.0	112.0	—	112.0	390.0	363.0
n-Butyl ether	9.4	73°F	12.7	13.8	21.0	19.5	—	53.8
		120°F	110.0	107.0	112.0	107.0	—	347.0
Ethyl acetate	12.0	73°F	3.9	3.7	4.5	5.2	14.8	11.2
		120°F	51.0	29.0	43.0	29.0	140.0	72.5
Acetone	13.8	73°F	1.5	1.5	1.9	2.1	0.7	3.9
		120°F	19.0	11.5	8.0	11.5	22.5	25.0
Acetic acid	15.5	73°F	—	0.6	1.0	0.9	—	1.4
		120°F	—	4.9	6.0	4.9	—	8.9
Methanol	17.5	73°F	0.3	0.2	0.2	0.3	0.2	0.4
		120°F	4.8	1.8	5.2	1.8	3.9	2.7

* Using Equation 3: log P-f = K − 0.22 π where K is 3.21 and 3.36 for Ziegler and Phillips at 73°F respectively and 4.10 for both at 120°F (see Figure 4)

** Using Equation 6: log P-f = K − 0.26 π where K is 4.17 at 73°F and 4.98 at 120°F for polypropylene (see Figure 5)

(The table shows that out of the 46 P-factors predicted 40 are doneee types of polymers is of the same order of accuracy as for regular points is only 20%. Thus, prediction of the permeabilities for these thr so within 30% accuracy and that the average percent error for all polyethylene for which the system was derived).

Table 7. Exceptions

Cause of Deviation	Direction of Deviation	EXAMPLES Liquid	Exp. P-f	Cal'd P-f
1. Perfect symmetry of polar groups cancels out any net polar charge	P-f increases	Hydroquinone	0.36	0.10
		CCl_4	610.0	500.0
2. Lower temperature decreases effective polarity of molecule	P-f increases	Methyl ethyl ketone	3.7 (32°F)	1.8
		Acetaldehyde	3.4 (32°F)	0.8
3. Lower temperature causes phenyl group to become more rigid and less able to mobilize.	P-f decreases	Benzaldehyde	0.37 (32°)	1.1
		Benzoic acid	0.07 (70°)	0.3
4. Chemical changes may take place at higher temperatures due to oxygen and moisture entering the permeant through the polyethylene	P-f increases or decreases	Acetic anhydride (forms some acetic acid which has a higher P-f)	213 (165°)	95
5. Intramolecular Hydrogen-bonding between segments of the same molecule essentially reduce the size of the permanent molecule	P-f increases	Diacetone alcohol	0.3 (70°)	0.01
		Diethylene glycol	0.76 (165°)	0.02
		Ethylene glycol	1.26 (165°)	0.2
		Ethylene glycol — monobutyl ether	180 (165°)	87
		Glycerin	1.6 (165°)	~0
6. Changing of shape factor with increasing temperature	P-f increases	sec-Butyl alcohol	278 (165°)	87
		tert-Butyl alcohol	236 (165°)	32

Solubility, Diffusion and Permachor Values

The classical method of treating permeability through a thin polymeric membrane at constant temperature is:

$$P\text{-}f = D\,S \qquad (7)$$

where

P-f is the permeability factor,
D is the diffusion constant of the permeant
and
S is the solubility of the permeant in the film

This states that permeability depends upon two physical factors—solubility and diffusion. There are many cases where one property is high for a given permeant while the other is quite low and the two properties cannot be directly related. Diffusion is very sensitive to the size and shape of the permeating molecule while solubility is dependent more so upon force constants between the solvating molecule and the polymer. Neither one of these properties can be correlated to size, shape or polarity alone. By a close examination of P-factors, solubilities and diffusion constants of over 40 organic liquids in polyethylene, it was found that neither S nor D correlated well alone with Permachor values while their product, which is P-f, correlates very well as is disclosed in this article. Of the two factors D correlates slightly better than S indicating that in general, diffusion rather than solubility, is the controlling factor in liquid permeability. Any attempt to correlate P-f with D alone, however, is unsuccessful. The Permachor method merely foregoes considering S and D alone and takes into account only the ultimate P-factor. The Permachor, then, can be considered a gross classification of the permeant taking into account its size, shape, polarity and interaction forces with polyethylene.

Exceptions

There are certain substances and groups of substances which give either much higher or lower P-factors at certain temperatures than would be predicted by their calculated Permachor values. Some of these exceptions along with the suspected cause of deviation and examples appear in *Table 7*. Most likely there are other causes of deviations not covered here, but these are the most evident.

Literature References

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2. Pinsky, J., Nielsen, A. R., and Parliman, J. H., Wright Air Development Center Technical Report 53-133, Vols. 1-4. Prepared by Plax Corp. under USAF Contract No. AF-33(616)-112 (1954-1955)
3. Bent, H. A., Pinsky, J., WADC Report 53-133, Vol. 2 (1955)
4. Bixler, H. J., "Solution and Flow of Gases in Polyethylene," ScD Thesis MIT (1959)

Appendix 1.

CALCULATED AND EXPERIMENTAL P-FACTORS FOR 79 ORGANIC COMPOUNDS IN REGULAR POLYETHYLENE AT 4 TEMPERATURES

PERMEANT	PERMACHOR τ (from Table 1)	P-FACTOR IN (GRAMS/24 HRS/.00 IN²/.001") 32°F		70°F		130°F		165°F	
		Exp.	Calc'd	Exp.	Calc'd	Exp.	Calc'd	Exp.	Calc'd
Hydrocarbons									
Benzene	5.4-7.6	45	65	440	600	4500	3800	13700	17000
Cyclohexane	7.0-8.0	31.6	29	251	270	3730	3100	15000*	14000
Decane	10.0	9.5	6.3	71.2	59	1220	1120	4120	5000
Dipentene	8.9	15	11	128	105	2030	2000	8110	8600
n-Heptane	7.0	48.6	29	270	270	2650	5000	8160	23000
n-Heptene	6.8	—	32	270**	300	—	5600	—	25000
n-Hexane	6.0	48	48	350	450	9000	8500	30000	38000
Methylcyclohexane	7.0	—	29	275	270	—	5000	—	23000
Octadecane	16.7	—	0.2	1.8**	2.0	—	40	—	160
i-Pentane	7.0	48	29	270	270	5000*	5000	20000*	23000
n-Pentane	5.0	97	80	526	740	15000*	14000	60000*	62000
Pentene-2	4.8	180	90	695	800	16000*	15000	65000*	70000
Tetradecane	13.0	1.7	1.4	14.6	13	404	250	1000*	1100
Tetradecene	12.8	—	1.5	12**	14	—	270	—	1200
Toluene	6.4	58	40	505	370	5775	7000	28700	31000
o-Xylene	7.4	36	24	256	230	3600	4100	16600	19000
p-Xylene	5.8-7.4	85.7	54	486	500	4800	4100	16300	19000

* Estimated from log P-f vs 1/T Plots.
** Estimated from cup tests.
Experimental P-factors taken from bottle test data from WADC Report,[2] calculated P-factors made using Eq. 3 and *Table 1*.

Appendix continued

PERMEANT	PERMACHOR π (from Table 1)	P-FACTOR IN (GRAMS/24 HRS/100 IN²/.001") 32°F Exp.	32°F Calc'd	70°F Exp.	70°F Calc'd	130°F Exp.	130°F Calc'd	165°F Exp.	165°F Calc'd
Halogenated Hydrocarbons									
Carbon Tetrachloride	5.8	51	54	610	500	7830	9200	45000	42000
Chlorobenzene	6.6	57.8	36	455	340	4410	6200	21150	28000
p-Chlorotoluene	6.0-7.6	30	48	304	450	4170	3800	18500	17000
1,2-Dibromo-ethane	8.0	—	17	140	160	—	3100	—	14000
o-Dichloro-benzene	7.8	—	19	155	180	—	3500	—	15000
1,1,1-Trichloro-ethane	5.6	—	60	260	550	—	10000	—	45000
Amines									
Aniline	16.4	0.25°	0.24	1.7	2.3	59.6	45	294	200
m-Chloroaniline	17.6	—	0.13	1.6	1.3	—	24	—	100
i-Propyl Amine	11.0	2.3	3.8	40.8	36	700°	680	3200°	3000
Amides									
Acetanilide	25.4	—	0.0025	0.02°	0.025	0.4	0.54	3.4	2.0
Formamide	19	—	0.065	0.5	0.6	—	12	—	52
Nitrates									
Nitrobenzene	15	0.37	0.5	4.9	4.7	100°	90	420°	400
Nitroethane	15.4	0.97	0.4	2.7	3.8	64	70	290	320
Nitromethane	16.4	—	0.24	2.1	2.3	—	45	—	190
Alcohols									
Allyl Alcohol	18.3	0.16	0.09	1.45	0.86	23	17	138	75
i-Amyl Alcohol	21	—	0.02	0.2°	0.22	—	43	—	19
Benzyl Alcohol	19.4	—	0.05	0.4	0.5	—	10	—	42
n-Butyl Alcohol	18	0.1°	0.11	0.46	1.0	20.4	20	150	87
s-Butyl Alcohol	18	0.12°	0.11	0.62	1.0	37.6	20	278	87
t-Butyl Alcohol	20	0.05°	0.04	0.26	0.36	27	7	236	32
Diethylene-Glycol	34	—	—	—	—	—	—	0.76	0.02
Ethyl Alcohol	18.5	—	0.07	0.7°°	0.76	—	15	—	67
2-Ethyl-Hexanol	20	—	0.04	0.3	0.36	—	7	—	32
Ethylene Glycol	30	—	0.0002	—	0.002	—	0.05	1.26	0.2
Ethylene Glycol-Monobutyl-Ether	18	—	0.11	0.67	1.0	35	20	180	87
Furfuryl Alcohol	20.6	—	0.03	0.24	0.27	—	5.2	—	23
Glycerin	49.5	—	—	—	—	0.36	—	1.6	~0
Heptyl Alcohol	18	—	0.11	1.0°°	1.0	—	20	—	87
Hydroquinone	31.4	—	—	—	—	0.06	0.02	0.36	0.10
Methyl Alcohol	17.5	0.25	0.14	1.22	1.3	27.8	25	100°	110
Octyl Alcohol	18	0.10	0.11	0.5	1.0	25.6	20	188	87
Phenol	18.4	0.10°	0.09	0.5	0.8	24	16	120	70
n-Propyl Alcohol	18.5	0.07	0.07	0.5	0.8	22.4	15	168	66

Appendix continued

PERMEANT	PERMACHOR π (from Table 1)	P-FACTOR IN (GRAMS/24 HRS/100 IN²/.001") 32°F Exp.	32°F Calc'd	70°F Exp.	70°F Calc'd	130°F Exp.	130°F Calc'd	165°F Exp.	165°F Calc'd
Acids									
Acetic Acid	15.5	0.35	0.39	3.1	3.6	66	69	304	310
Benzoic Acid	20.4	—	0.03	0.07	0.3	5.7	6	36	25
n-Butyric-Acid	15	0.19	0.5	4.8	4.7	100*	90	580	400
Chloroacetic Acid	16.7	—	0.2	0.3	2.0	15	38	60	170
Formic Acid	19	0.25	0.07	0.67	0.6	12	12	51	52
Oxalic Acid	29	—	0.0004	—	0.004	0.2	0.07	0.23	0.3
Anhydrides									
Acetic Anhydride	17.8	0.13*	0.12	0.81	1.1	29.6	21	213	95
Chloromaleic-Anhydride	23	—	0.01	0.07	0.08	—	1.6	—	7
Ethers									
Dibutyl Ether	9.4	11.2	8.5	85.5	80	1480	1500	3140	6700
Diethyl Ether	6.4	48	40	313	370	8000*	7000	30000*	31000
Esters									
Amyl Acetate	14	0.56	0.8	8.7	7.8	269	160	1095	660
i-Amyl-Propionate	13.1	—	1.3	10**	12	—	230	—	1000
n-Amyl-Propionate	11.1	—	3.5	30**	34	—	620	—	2800
n-Butyl Acetate	13	—	1.4	15**	13	—	250	—	1100
Dibutyl-Phthalate	20.9	—	0.02	—	0.23	5.7	4.5	27.8	20
Diethyl-Oxalate	19.2	—	0.06	0.7	0.6	—	11	—	48
Ethyl Acetate	12	1.9	2.3	16.5	22	378	400	1703	1800
Ethyl-Propionate	12	—	2.3	25**	22	—	400	—	1800
Ethyl Formate	12.6	—	1.7	15**	16	—	300	—	1300
n-Heptyl-Acetate	12.1	—	2.2	18**	20	—	380	—	1700
Methyl-Acetate	12.6	—	1.7	14**	16	—	300	—	1300
Ketones									
Acetone	13.8	1.4	0.9	6.8	8.5	184	160	750*	720
Camphor	17.8	—	0.12	0.3	1.1	21.5	21	162	95
Methyl Ethyl-ketone	12.5	3.7	1.8	12.6	17	326	320	1401	1400
Aldehydes									
Acetaldahyde	14	3.4	0.8	6	8	—	150	—	650
Benzaldehyde	14.4	0.37	0.67	6.8	6.3	206	120	1060	540
Butyraldehyde	13.5	0.9	1.0	10	10	584	190	1000*	850
Formaldehyde	18.8	—	0.07	0.53	0.68	—	13	—	58
Mercaptans									
Ethyl-Mercaptan	6	26	48	400	450	10000*	8500	40000*	38000

The Thermodynamics of Biaxial Elongation*

Biaxial orientation of film is becoming increasingly important. Thermodynamics of this phenomenon, of interest from a point of view, of molecular interpretation are examined here

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The change in entropy, S, and internal energy, E, upon simple elongation of a solid may be obtained using the equations

$$\left[\frac{\partial S}{\partial l}\right]_{V,T} = -\left[\frac{\partial f}{\partial T}\right]_{l,V} \qquad (1)$$

and

$$\left[\frac{\partial E}{\partial l}\right]_{V,T} = f - T\left[\frac{\partial f}{\partial T}\right]_{l,V} \qquad (2)$$

(where f is the force, l the length, V the volume, and T the absolute temperature). The form of these equations was first realized by Joule (1) and their application to rubbers has been extensively investigated by a number of workers (2, 3, 4). It was realized that few experiments were carried out at constant volume, and that a correction term was necessary for constant pressure experiments (5, 6, 7), shown in equation 3.

$$\left[\frac{\partial E}{\partial l}\right]_{V,T} \cong f - T\left[\frac{\partial f}{\partial T}\right]_{P,\epsilon} + \alpha l T\left[\frac{\partial f}{\partial l}\right]_{P,T} \qquad (3)$$

where α is the coefficient of linear expansion of the unstretched material, and ϵ is the strain. This equation is an approximation since it does not allow for anisotropy of the thermal expansion and moduli of the material.

Extension to Biaxial Elongation

The extension of the thermodynamic analysis to the case of two-dimensional deformation is of interest in

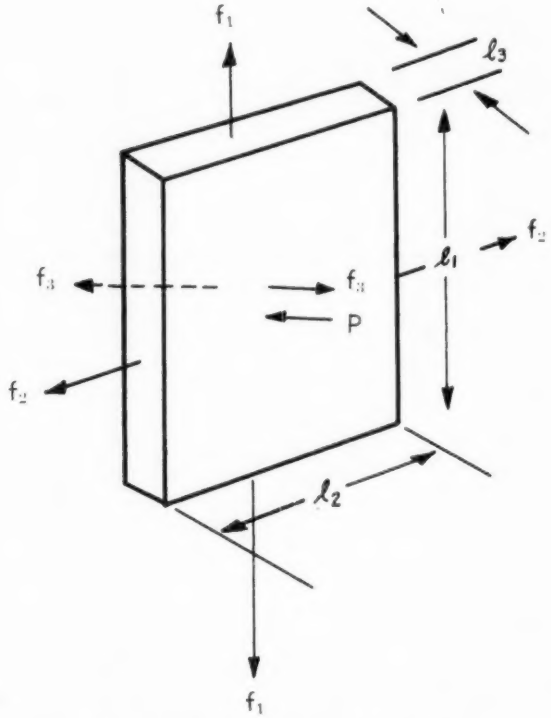

Figure 1. A Sample in Two-Dimensional Elongation

* Supported in part by a contract from the Office of Naval Research and in part by: grants from the National Science Foundation, the Plax Corporation and assistance from the Monsanto Chemical Company.

elucidating the molecular mechanisms of such processes. In this case two lengths must be specified to characterize the state of the material. l_1 and l_2 will be used to designate the dimensions of a film of material in its plane and l_3 to designate the thickness perpendicular to its plane. (*Figure 1*). Thus, the internal energy change of the film is

$$dE = q - w$$
$$= TdS - PdV + f_1\,dl_1 + f_2\,dl_2 \qquad (4)$$

for a reversible process, f_1 and f_2 are forces in the directions of l_1 and l_2 (assumed to be the principal stress directions). Then

$$dA = dE - TdS - SdT$$
$$= -PdV - SdT + f_1\,dl_1 + f_2\,dl_2 \qquad (5)$$

so

$$P = -\left[\frac{\partial A}{\partial V}\right]_{T,l_1,l_2} \qquad (6)$$

$$S = -\left[\frac{\partial A}{\partial S}\right]_{V,l_1,l_2} \qquad (7)$$

$$f_1 = \left[\frac{\partial A}{\partial l_1}\right]_{T,V,l_2}$$

and

$$f_2 = \left[\frac{\partial A}{\partial l_2}\right]_{T,V,l_1} \qquad (8)$$

By differentiating a second time and equating identical second derivatives, the following Maxwell type equations may be obtained

$$\left[\frac{\partial P}{\partial T}\right]_{V,l_1,l_2} = \left[\frac{\partial S}{\partial V}\right]_{T,l_1,l_2} \qquad (9)$$

$$\left[\frac{\partial f_1}{\partial T}\right]_{V,l_1,l_2} = -\left[\frac{\partial S}{\partial l_1}\right]_{T,V,l_2} \qquad (10)$$

$$\left[\frac{\partial f_2}{\partial T}\right]_{V,l_1,l_2} = -\left[\frac{\partial S}{\partial l_2}\right]_{T,V,l_1} \qquad (11)$$

$$\left[\frac{\partial f_1}{\partial V}\right]_{T,l_1,l_2} = -\left[\frac{\partial P}{\partial l_1}\right]_{T,V,l_2} \qquad (12)$$

$$\left[\frac{\partial f_2}{\partial V}\right]_{T,l_1,l_2} = -\left[\frac{\partial P}{\partial l_2}\right]_{T,V,l_1} \qquad (13)$$

By substituting (10) in equation (14)

$$f_1 = \left[\frac{\partial A}{\partial l_1}\right]_{T,V,l_2} = \left[\frac{\partial E}{\partial l_1}\right]_{T,V,l_2} - T\left[\frac{\partial S}{\partial l_1}\right]_{T,V,l_2} \qquad (14)$$

one obtains

$$\left[\frac{\partial E}{\partial l_1}\right]_{T,V,l_2} = f_1 - T\left[\frac{\partial f_1}{\partial T}\right]_{V,l_1,l_2} \qquad (15)$$

Similarly, from equation (11), it follows that

$$\left[\frac{\partial E}{\partial l_2}\right]_{T,V,l_1} = f_2 - T\left[\frac{\partial f_2}{\partial T}\right]_{V,l_1,l_2} \qquad (16)$$

Consequently, if the temperature variations of the forces in two principal directions are observed simultaneously at constant sample dimensions, the internal energy and entropy changes on elongation in those directions may be calculated. It is of interest to determine how such changes in a two-dimensional elongation compare with those for a simple elongation, as well as how the thermodynamic changes in one direction are affected by the state of elongation in the second direction.

Expressions in Terms of Stresses and Strains

One is usually interested in sample variables expressed in a form independent of the sample dimensions. The internal energy and entropy per unit initial volume will be defined as follows

$$\overline{E}_{T_1} = \frac{E}{V_o,T_1} = \frac{E}{l_{10}\,l_{20}\,l_{30}} \qquad (17)$$

$$\overline{S}_{T_1} = \frac{S}{V_o,T_1} = \frac{S}{l_{10,T_1}\,l_{20,T_1}\,l_{30,T_1}} \qquad (18)$$

where T_1 signifies the temperature of measurement, V_o,T_1 is the volume at this temperature at zero deformation, and l_{10}, l_{20}, and l_{30} are the three principal dimensions corresponding to this volume.

The stresses and strains relative to the original dimensions are defined as

$$\sigma_{10} = \frac{f_1}{l_{20,T_1}\,l_{30,T_1}} \qquad (19)$$

$$\sigma_{20} = \frac{f_2}{l_{10,T_1}\,l_{30,T_1}} \qquad (20)$$

$$\epsilon_{10} = \frac{l_1 - l_{10,T_1}}{l_{10,T_1}} \qquad (21)$$

$$\epsilon_{20} = \frac{l_2 - l_{20,T_1}}{l_{20,T_1}} \qquad (22)$$

By substituting these definitions in equations (10), (11), (15) and (16) one obtains

$$\left[\frac{\partial \overline{S}_{T_1}}{\partial \epsilon_{10}}\right]_{T_1,V,\epsilon_{20}} = -\left[\frac{\partial \sigma_{10}}{\partial T}\right]_{V,\epsilon_{10},\epsilon_{20}} \qquad (23)$$

$$\left[\frac{\partial \overline{S}_{T_1}}{\partial \epsilon_{20}}\right]_{T_1,V,\epsilon_{10}} = -\left[\frac{\partial \sigma_{20}}{\partial T}\right]_{V,\epsilon_{10},\epsilon_{20}} \qquad (24)$$

$$\left[\frac{\partial \overline{E}_{T_1}}{\partial \epsilon_{10}}\right]_{T_1,V,\epsilon_{20}} = \sigma_{10} - T_1\left[\frac{\partial \sigma_{10}}{\partial T}\right]_{V,\epsilon_{10},\epsilon_{20}} \qquad (25)$$

$$\left[\frac{\partial \overline{E}_{T_1}}{\partial \epsilon_{20}}\right]_{T_1,V_1,\epsilon_{10}} = \sigma_{20} - T_1\left[\frac{\partial \sigma_{20}}{\partial T}\right]_{V,\epsilon_{10},\epsilon_{20}} \qquad (26)$$

The condition of constant volume in the term $(\partial\sigma_{10}/\partial T)_{V,\epsilon_{10},\epsilon_{20}}$ requires that the thickness be kept constant as the temperature is varied. This would be difficult experimentally. The more common experimental condition is that of constant pressure. The following section is devoted to the calculation of thermodynamic functions from data obtained in such experiments.

Biaxial Elongation at Constant Pressure

In constant pressure experiments, one may proceed in the analogous manner using the Gibbs' free energy:

$$dF = dA + PdV + VdP \tag{27}$$
$$= VdP + f_1 d\,l_1 + f_2 d\,l_2 - SdT$$

This gives

$$V = \left[\frac{\partial F}{\partial P}\right]_{T,l_1,l_2} \tag{28}$$

$$S = -\left[\frac{\partial F}{\partial T}\right]_{P,l_1,l_2} \tag{29}$$

$$f_1 = \left[\frac{\partial F}{\partial l_1}\right]_{T,P,l_2} \tag{30}$$

$$f_2 = \left[\frac{\partial F}{\partial l_2}\right]_{T,P,l_1} \tag{31}$$

The resulting "Maxwell Equations" are

$$\left[\frac{\partial V}{\partial T}\right]_{P,l_1,l_2} = -\left[\frac{\partial S}{\partial P}\right]_{T,l_1,l_2} \tag{32}$$

$$\left[\frac{\partial f_1}{\partial T}\right]_{P,l_1,l_2} = -\left[\frac{\partial S}{\partial l_1}\right]_{T,P,l_2} \tag{33}$$

$$\left[\frac{\partial f_2}{\partial T}\right]_{P,l_1,l_2} = -\left[\frac{\partial S}{\partial l_2}\right]_{T,P,l_1} \tag{34}$$

$$\left[\frac{\partial T_1}{\partial P}\right]_{T,l_1,l_2} = \left[\frac{\partial V}{\partial l_1}\right]_{P,T,l_2} \tag{35}$$

$$\left[\frac{\partial f_2}{\partial P}\right]_{T,l_1,l_2} = \left[\frac{\partial V}{\partial l_2}\right]_{P,T,l_1} \tag{36}$$

From

$$dF = dH - TdS - SdT \tag{37}$$

and equations (30), (31), (33) and (34), one obtains

$$\left[\frac{\partial H}{\partial l_1}\right]_{T,P,l_2} = f_1 - T\left[\frac{\partial f_1}{\partial T}\right]_{P,l_1,l_2} \tag{38}$$

and

$$\left[\frac{\partial H}{\partial l_2}\right]_{T,P,l_2} = f_2 - T\left[\frac{\partial f_2}{\partial T}\right]_{P,l_1,l_2} \tag{39}$$

In terms of unit volume quantities, the corresponding equations are

$$\left[\frac{\partial \overline{S}_{T_1}}{\partial \epsilon_{10}}\right]_{T_1,P,\epsilon_{20}} = -\left[\frac{\partial \sigma_{10}}{\partial T}\right]_{P,\epsilon_{10},\epsilon_{20}} \tag{40}$$

$$\left[\frac{\partial \overline{S}_{T_1}}{\partial \epsilon_{20}}\right]_{T_1,P,\epsilon_{10}} = -\left[\frac{\partial \sigma_{20}}{\partial T}\right]_{P,\epsilon_{10},\epsilon_{20}} \tag{41}$$

$$\left[\frac{\partial \overline{H}_{T_1}}{\partial \epsilon_{10}}\right]_{T_1,P,\epsilon_{20}} = \sigma_{10} - \left[\frac{\partial \sigma_{10}}{\partial T}\right]_{P,\epsilon_{10},\epsilon_{20}} \tag{42}$$

$$\left[\frac{\partial \overline{H}_{T_2}}{\partial \epsilon_{20}}\right]_{T_1,P,\epsilon_{10}} = \sigma_{20} - \left[\frac{\partial \sigma_{20}}{\partial T}\right]_{P,\epsilon_{10},\epsilon_{20}} \tag{43}$$

Relationship Between Constant Volume and Constant Pressure Quantities

The above thermodynamic quantities at constant pressure reflect two types of changes:

1. Those resulting from configurational changes accompanying extension, and
2. Those resulting from volume changes accompanying pressure, and
   a. Compressional work done against the external pressure, and
   b. Potential changes involved in separating atoms and molecules of the material from each other as the volume increases.

The volume changes on elongation may be a consequence of:

1. The hydrostatic component of tension.
2. Phase changes such as crystallization involving a volume change.
3. Void formation or cavitation.

The thermodynamic derivatives obtained at constant volume however are related only to the configurational changes, and are of more fundamental interest from a molecular interpretation point of view. Consequently, it is desirable to transform the constant-pressure quantities into constant volume ones.

By differentiating the equation

$$H = E + PV \tag{44}$$

$$\left[\frac{\partial H}{\partial l_1}\right]_{T,P,l_2} = \left[\frac{\partial E}{\partial l_1}\right]_{T,P,l_2} + P\left[\frac{\partial V}{\partial l_1}\right]_{T,P,l_2} \tag{45}$$

Since E may be expressed as a function of V,T,l_1 and l_2,

$$dE = \left[\frac{\partial E}{\partial l_1}\right]_{V,T,l_2} dl_1 + \left[\frac{\partial E}{\partial l_2}\right]_{V,T,l_1} dl_2 + \left[\frac{\partial E}{\partial V}\right]_{T,l_1,l_2} dV + \left[\frac{\partial E}{\partial T}\right]_{V,l_1,l_2} dT \tag{46}$$

so

$$\left[\frac{\partial E}{\partial l_1}\right]_{T,P,l_2} = \left[\frac{\partial E}{\partial l_1}\right]_{V,T,l_2} + \left[\frac{\partial E}{\partial V}\right]_{T,l_1,l_2}\left[\frac{\partial V}{\partial l_1}\right]_{T,P,l_2} \tag{47}$$

On substituting into (45) one obtains

$$\left[\frac{\partial H}{\partial l_1}\right]_{T,P,l_2} = \left[\frac{\partial E}{\partial l_1}\right]_{V,T,l_2} + \left\{P + \left[\frac{\partial E}{\partial V}\right]_{T,l_1,l_2}\right\}\left[\frac{\partial V}{\partial l_1}\right]_{T,P,l_2} \tag{48}$$

To evaluate $(\partial E/\partial V)_{T,l_1,l_2}$ we differentiate equation (4)

$$\left[\frac{\partial E}{\partial V}\right]_{T,l_1,l_2} = T\left[\frac{\partial S}{\partial V}\right]_{T,l_1,l_2} - P \tag{49}$$

which gives, using equation (9)

$$\left[\frac{\partial E}{\partial V}\right]_{T,l_1,l_2} = T\left[\frac{\partial P}{\partial T}\right]_{V,l_1,l_2} - P \tag{50}$$

On substituting into (48), this gives

$$\left[\frac{\partial H}{\partial l_1}\right]_{T,P,l_2} = \left[\frac{\partial E}{\partial l_1}\right]_{V,T,l_2} - T\left[\frac{\partial P}{\partial T}\right]_{V,l_1,l_2}\left[\frac{\partial V}{\partial l_1}\right]_{T,P,l_2} \quad (51)$$

By combining with equation (38), one gets

$$\left[\frac{\partial \bar{E}}{\partial l_1}\right]_{V,T,l_2} = f_1 - T\left[\frac{\partial f_1}{\partial T}\right]_{P,l_1,l_2} + T\left[\frac{\partial P}{\partial T}\right]_{V,l_1,l_2}\left[\frac{\partial V}{\partial l_1}\right]_{T,P,l_2} \quad (52)$$

in terms of unit volume quantities, this is

$$\left[\frac{\partial \bar{E}_{T_1}}{\partial \epsilon_{10}}\right]_{V,T_1,\epsilon_{10}} = \sigma_{10} - T_1\left[\frac{\partial \sigma_{10}}{\partial T}\right]_{P,\epsilon_{10},\epsilon_{20}} + \frac{T_1}{V_o}\left[\frac{\partial P}{\partial T}\right]_{V_1,\epsilon_{10},\epsilon_{20}}\left[\frac{\partial V}{\partial \epsilon_{10}}\right]_{T_1,P,\epsilon_{20}} \quad (53)$$

Similarly for direction 2,

$$\left[\frac{\partial \bar{E}_{T_1}}{\partial \epsilon_{20}}\right]_{V,T_1,\epsilon_{10}} = \sigma_{20} - T_1\left[\frac{\partial \sigma_{20}}{\partial T}\right]_{P,\epsilon_{10},\epsilon_{20}} + \frac{T_1}{V_o}\left[\frac{\partial P}{\partial T}\right]_{V_1,\epsilon_{10},\epsilon_{20}}\left[\frac{\partial V}{\partial \epsilon_{20}}\right]_{T_1,P,\epsilon_{20}} \quad (54)$$

Thus, one may obtain the constant volume derivatives from a constant pressure experiment if the third correctional term can be evaluated. For a sample having strictly constant volume, $(\partial V/\partial \epsilon_{10})_{T_1,P,\epsilon_{20}} = 0$, the third term vanishes.

Evaluation of the Correction Term

To evaluate $(\partial P/\partial T)_{V_1,\epsilon_{10},\epsilon_{20}}$, V is expressed as a function of the stated variables l_1, l_2, P, and T

$$dV = \left[\frac{\partial V}{\partial l_1}\right]_{l_2,P,T} dl_1 + \left[\frac{\partial V}{\partial l_2}\right]_{l_1,P,T} dl_2 + \left[\frac{\partial V}{\partial P}\right]_{T,l_1,l_2} dP + \left[\frac{\partial T}{\partial T}\right]_{P,l_1,l_2} dT \quad (55)$$

At constant V, ϵ_{10}, ϵ_{20}, $dV = dl_1 = dl_2 = 0$
so that (55) gives

$$\left[\frac{\partial P}{\partial T}\right]_{V,\epsilon_{10},\epsilon_{20}} = -\frac{\left[\frac{\partial V}{\partial T}\right]_{P,\epsilon_{10},\epsilon_{20}}}{\left[\frac{\partial V}{\partial P}\right]_{T,\epsilon_{10},\epsilon_{20}}} \quad (56)$$

Define the thermal expansion coefficient at constant biaxial elongation as α_ϵ where

$$\alpha_\epsilon = \frac{1}{V}\left[\frac{\partial V}{\partial T}\right]_{P,\epsilon_{10},\epsilon_{20}} \quad (57)$$

$$= \frac{1}{l_1 l_2 l_3}\left[\frac{\partial (l_1 l_2 l_3)}{\partial T}\right]_{P,l_1,l_2} = \frac{1}{l_3}\left[\frac{\partial l_3}{\partial T}\right]_{P,l_1,l_2} \quad (58)$$

This is identical with the linear expansion coefficient for change in thickness for a sample held at constant area. The isothermal compressibility, β_ϵ, for a sample at constant biaxial elongation is defined as

$$\beta_\epsilon = -\frac{1}{V}\left[\frac{\partial V}{\partial P}\right]_{T,\epsilon_{10},\epsilon_{20}} = -\frac{1}{l_1 l_2 l_3}\left[\frac{\partial (l_1 l_2 l_3)}{\partial P}\right]_{T,l_1,l_2} = -\frac{1}{l_3}\left[\frac{\partial l_3}{\partial P}\right]_{T,l_1,l_2} \quad (59)$$

For a sample in the form of an elongated film, the pressure is approximately equal to the negative of the normal stress perpendicular to the surface of the film σ_3; thus

$$\beta_\epsilon = \left[\frac{\partial \epsilon_3}{\partial \sigma_{30}}\right]_{T,l_1,l_2} = \frac{1}{(M_{33})_\epsilon} \quad (60)$$

where $(M_{33})_\epsilon$ is the Young's Modulus normal to the film held at constant area.

Therefore

$$\left[\frac{\partial P}{\partial T}\right]_{V,\epsilon_{10},\epsilon_{20}} = \frac{\alpha_\epsilon}{\beta_\epsilon} = -\alpha_\epsilon (M_{33})_\epsilon \quad (61)$$

The term $(\partial V/\partial l_1)_{T,P,l_2}$ is evaluated in a similar manner by expressing P as a function of l_1, l_2, V, and T which leads to

$$\left[\frac{\partial V}{\partial l_1}\right]_{T,P,l_2} = -\frac{\left[\frac{\partial P}{\partial l_1}\right]_{V,T,l_2}}{\left[\frac{\partial P}{\partial V}\right]_{T,l_1,l_2}} \quad (62)$$

The denominator is related to the compressibility. The numerator depends upon the anisotropy of the sample. For films where $P \cong -\sigma_3$

$$\left[\frac{\partial P}{\partial l_1}\right]_{V,T,l_2} = -\left[\frac{\partial \sigma_3}{\partial l_1}\right]_{V,T,l_2} = -\frac{1}{l_1}\left[\frac{\partial \sigma_3}{\partial \epsilon_{10}}\right]_{V,T,l_2} = -\frac{1}{l_1}(M_{31})_{\epsilon_2} \quad (63)$$

M_{31} is a non-diagonal component of the modulus tensor which expresses how much a stress normal to the surface causes the length of the film to increase.

$$[M_{31}]_{\epsilon_2} = \left[\frac{\partial \sigma_3}{\partial \epsilon_{30}}\right]_{V,T,l_2}\left[\frac{\partial \epsilon_{30}}{\partial \epsilon_{10}}\right]_{V,T,l_2} \quad (64)$$

$(\partial \epsilon_{30}/\partial \epsilon_{10})_{V,T,l_2}$ is like a Poisson's ratio but for an anisotropic film and expresses the ratio of thickness to length increase at constant volume and width.

Since

$$V = l_1 l_2 l_3 \quad (65)$$

At constant volume

$$dV = l_{20} l_{30} dl_1 + l_{10} l_{30} dl_2 + l_{10} l_{20} dl_3 = 0 \quad (66)$$

$$= \frac{dl_1}{l_{10}} + \frac{dl_2}{l_{20}} + \frac{dl_3}{l_{30}} = 0$$

$$d\epsilon_{10} + d\epsilon_{20} + d\epsilon_{30} = 0 \quad (67)$$

If l_2 is constant, $d\epsilon_{20} = 0$ and

$$\left[\frac{\partial \epsilon_{30}}{\partial \epsilon_{10}}\right]_{V,T,l_2} = -1 \quad (68)$$

so

$$[M_{31}]_{\epsilon_2} = \left[\frac{\partial \sigma_{30}}{\partial \epsilon_{30}}\right]_{V,T,l_2} = -[M_{33}]_{\epsilon_{20}} \quad (69)$$

and

$$\left[\frac{\partial P}{\partial l_1}\right]_{V,T,l_2} = +\frac{1}{l_1}[M_{33}]_{\epsilon_{20}} \quad (70)$$

$(M_{33})_{\epsilon_2}$ is the Young's Modulus perpendicular to the film held at constant width.

By combining Equations (54), (61), (62), (63), and (70) one obtains

$$\left[\frac{\partial \overline{E_{T_1}}}{\partial \epsilon_{10}}\right]_{V,T,\epsilon_{20}} = \sigma_{10} - T_1\left[\frac{\partial \sigma_{10}}{\partial T}\right]_{P,\epsilon_{10},\epsilon_{20}} + T_1 \alpha_\epsilon [M_{33}]_{\epsilon_2} \quad (71)$$

Similarly, in the second direction

$$\left[\frac{\partial \overline{E_{T_1}}}{\partial \epsilon_{20}}\right]_{V,T,\epsilon_{10}} = \sigma_{20} - T_1\left[\frac{\partial \sigma_{20}}{\partial T}\right]_{P,\epsilon_{10},\epsilon_{20}} + T_1 \alpha_\epsilon [M_{33}]_{\epsilon_1} \quad (72)$$

To the approximation that $\alpha_\epsilon \cong \alpha$ and $(M_{33})_{\epsilon_1} = M$ (the average Young's Modulus), these equations reduce to the simpler case discussed by previous workers (3, 7).

The entropy of elongation is corrected by a similar procedure and is

$$\left[\frac{\partial \overline{S_{T_1}}}{\partial \epsilon_{10}}\right]_{V,T,\epsilon_{20}} = -\left[\frac{\partial \sigma_{10}}{\partial T}\right]_{P,\epsilon_{10},\epsilon_{20}} + \alpha_\epsilon [M_{33}]_{\epsilon_2} \quad (73)$$

$$\left[\frac{\partial \overline{S_{T_1}}}{\partial \epsilon_{20}}\right]_{V,T,\epsilon_{10}} = -\left[\frac{\partial \sigma_{20}}{\partial T}\right]_{P,\epsilon_{10},\epsilon_{20}} + \alpha_\epsilon [M_{33}]_{\epsilon_1} \quad (74)$$

The measurement of α_ϵ, $(M_{33})_{\epsilon_2}$ and $(M_{33})_{\epsilon_1}$ presents experimental problems. α_ϵ could possibly be measured by an optical measurement of the change in distance between the surfaces of the film.

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Polymers as Conductors and Semi-conductors

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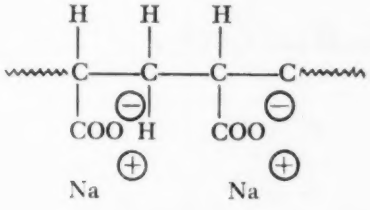
Methods for preparing semi conductive polymers are:

- *Introduction of mobile ions (conductance by ion pairs)*
- *Introduction of mobile electrons (polymers with conjugated double bonds)*
- *Preparation of polymers with metallo-cyclics in the chain of conjugation*
- *Preparation of conjugated polymers containing heteroatoms*

This article is a review of conductive and semi-conductive properties of polymeric materials. The four methods of preparing semi-conducting polymers are outlined below.

Introducing Mobile Ions

In a carboxyl containing polyethylene chain at high pH the proton may be removed from the carboxyl group leaving a negative charge on the chain with a "free" sodium ion near the parent carboxyl group.



One can also use sulfoxyl groups or any kind of dissociable groups which form acids and bases. Thus, one can have a concentrated salt solution, or an acid, or a base in solid form. This may be in the form of a fiber, a film or as a bulk material.

An important factor is the localization of the ions which cannot readily diffuse away. However, the mobility of the ions may be regulated by temperature and by the addition of plasticizers or swelling agents. These plasticizers fill in the spaces between the polymer chains and increase the mobility of the ions.

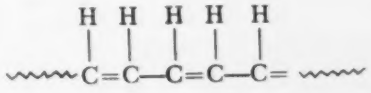
By these procedures it is possible to increase the conductivity of some polymers to form semi-conductors and even conductors for low frequency operation. Concentration as high as 10^{19} ions per cc can be achieved by putting one of these groups on each available carbon atom. A limiting factor for these solid polar electrolytes is temperature, since they cannot be used above 200°-250°C for any prolonged period without appreciable deterioration occurring. Materials of this type are being used in technology of storage batteries.

Another approach to this problem was made by research workers at University College, London. Organic polymers that conduct electricity have been synthesized by polymerizing bicyclopentyl derivatives obtained by a modified Diels-Alder reaction with dienes.

These polymers, darkly colored, conduct current in non-polar solvents in the presence of acid: they might also be conductive in the solid state. Basis for the polymers' electrical properties is conductance by ion-pairs formed during proton transfer from the acid to the conjugated bond system in the polymers. Using cyclopentadiene in the presence of trichloroacetic acid as a catalyst, the product was found to be a trichloroacetic acid ester of 3-(cyclopenta-2', 4'-dienyl) cyclopentanol.

Method of Synthesis of Polymeric Semi-conductors by Introduction of Electrons

The second method for increasing the conductivity of a polymeric structure is by increasing its electronic conductance. In polyethylene, each bond is formed by a pair of electrons. The energy to remove these electrons is very high, in order of 3-5 e.v. However, one can remove adjacent hydrogen atoms and thus form a series of conjugated double bonds



The orbitals of the electrons forming the second bond in a polymer with conjugated double bonds are much further away from the carbon nuclei and thus the electrons are more easily removed. As the number of double bonds increases the lower is the binding energy of these electrons. This decrease is due to the phenomenon of resonance, that is, essentially by the overlapping of the eigenfunctions for these various bonds. Calculations based on the potential energies involved indicate that very long chains of conjugated double bonds should have essentially metallic conductivity.

A general characteristic feature of such materials is the large degree of π-electrons which causes a decrease of the internal energy of the system and a decrease of the excitation energy of π-electrons into the triplet state owing to decrease in the energy difference between the highest occupied level and the lowest free electron level. Experimental data, presently available, permit conformation that properties of polymers with conjugated bonds depend on the length and structure of the chain of conjugation, on the nature and degree of conjugation of lateral groups on the presence of heteroatoms in the chain and on the physical character of the polymer.

A distinctive trait of polymers with conjugated double bonds (polyvinylenes) is limitation of rotational freedom around the C = C bond which stabilizes the arrangement of all links. Lengthening the chain of conjugation increases the number of possible structural isomers, which leads to a large variety of conformal structures.

Synthesis of polyvinylenes can be accomplished by the following methods:

a. Polycondensation
b. Polymerization of acetylene and its derivatives
c. Intermolecular cleavage by various physical or chemical interactions on polyvinylalcohol and halogen containing carbochain polymers

a. Polycondensation Methods

It was possible to synthesize oligomers with up to 12 to 15 conjugated double bonds by polycondensation methods (1)

b. Polymerization and Copolymerization of Acetylene and its derivatives

Conversion of alkyl and acrylacetylenes into corresponding polyvinylenes takes place at room or slightly higher temperature (40° to 70°C) in the presence of a catalyst of ionic or steroregular (complexes of $R_3Al + TiCl_3$) polymerization (2.3). Phenylacetylene is easily polymerized at 150°C with formation of soluble yellow or dark colored, nearly black, polymers with a molecular weight around 1100-1500 (2). Polyarylacetylene (polyphenylacetylene, polytolane) show narrow EPR signals characteristic of unpaired electrons along the chain of conjugation (10^{17} to 10^{19} paramagnetic particles per gram) and comparatively high values of the magnetic susceptibility (around 1.3×10^{-6}). Magnetic susceptibility and intensity of the EPR spectra increase on heating the samples to 300-400°C and as a rule increase with deepening of the color and consequent increasing length of the chain of conjugation. EPR and infrared data on polyphenylacetylenes conform completely with the appearance of uninterrupted π-electron conjugation: (see *Table 1*).

c. Intramolecular Cleavage by Various Physical or Chemical Interactions on Polyvinylalcohol Halogen Containing Vinyl Polymer or Acrylonitrile.

Together with synthetic methods of obtaining polyvinylenes, attention of investigators is drawn to methods based on intramolecular abstraction of atoms from saturated molecules. For this purpose most useful are polyvinylalcohol and various polyvinyl esters which are dissociated by thermal, photo, or radiation interaction without rupture of the chain (4).

Polyvinylene may be prepared by removing HB_r from polyvinylbromide after the polyvinylbromide has been formed into the desired shape or form such as a fiber or film. Preparation of soluble polyvinylene is very easily brought about by removal of HB_r from polyvinylbromide by the action of alcoholic alkali or organic bases. Polyvinylenes, colored in dark brown tones, which are formed in these reactions are characterized by nega-

Table 1. Properties of the Products of Thermal and Catalytic Polymerization of Phenylacetylene

Polymerization Conditions		Polymer yield (% on monomer)				Elemental Composition, %						
Temperature, °C.	Time, hours	in argon	in air	Polymer color	Polymer solubility	C	H	Softening Temp., °C.	No. of paramagnetic particles per g.	Specific magnetic susceptibility, χ*	M av.**	Specific viscosity of 2.5% solution in benzene
150	6	20	45	Yellow	acetone, benzene	93.87	6.13	175-180	2.4×10^{17}	-0.34×10^{-6}	1100	0.08
300	6	30	60	Brown	acetone, benzene	94.12	5.88	185-190	4.3×10^{18}	-0.43×10^{-6}	—	0.13
400	6	26	27	Brown	acetone, benzene	94.84	5.16	185-190	4.2×10^{18}	-0.43×10^{-6}	1300	0.14
		7	12	Black	benzene	94.84	5.16	-400	3.4×10^{19}	1.3×10^{-6}	1500	—
701	6	30	—	Yellow	acetone, benzene	93.00	7.00	160-170	8.8×10^{17}	—	—	0.08

* Tests carried out in the presence of $Al(Et)_3 + TiCl_4$
** Determined by the isopiestic method

Table 2. The D.C. Resistivities of Pyrolysis Products From Pre-Oxidized Polydivinylbenzene

Pyrolysis Temp.	Empirical formula of residues	Resistivity ohm cm 25°
500	$C_{26}H_{17}O$	10^{15}
600	$C_{34}H_{13}O$	10^{12}
700	$C_{45}H_{10}O$	10^{6}
1000	~0.6% H	10^{-2}

tive temperature coefficients of electrical resistance (5).

In the laboratories of the International Resistance Corporation work was conducted on conversion of polyvinylidene chloride and its copolymers into polyvinylenes (6).

Removal of HCl was accomplished by heating to boiling with morpholine or alcoholic alkali under vacuum in an atmosphere of N_2. As a result of such treatment, darkly-colored insoluble polymers are obtained with a specific magnetic susceptibility (X) of 1.56×10^{-6} corresponding to 1 free electron per every 18 carbon atoms along the chain of conjugation. Also, Winslow and collaborators (7) have shown that as a result of thermal treatment of polyvinylidene chloride and preoxydized polydivinylbenzene products are obtained which possess semi-conductive properties. Measurements of paramagnetic resonance absorption show close correlation among composition, semi-conductivity and odd electron concentration of these compounds.

The properties of these pyrolytic derivatives presumably result from extensive conjugation in a dense rigid carbon-carbon primary valence bond mesh. The low energies seemingly involved in providing conduction carriers lead to suggestion about electron movement in aromatic compounds. The sharp decrease in electrical resistance (*Table 2 and Figure 1*) with rising temperatures for the products of dehydrochlorination of polyvinylidene chloride allows one to view these substances as weak semi-conductors with high energy of activation, conductivity and significant value of specific resistivity at room temperature.

F. H. Winslow and collaborators, (7), of Bell Telephone Laboratories have studied the variation of resistivity of preoxydized polydivinyl benzene and polyvinylidene chloride as a function of the temperature at which pyrolysis was carried out, as shown in *Table 2 and Figure 1*. As more hydrogen is removed, the number of double bonds increases as well as the number of free electrons and the dc conductivity increases markedly when the pyrolysis temperature is increased above 600°C (a semi-conductor level of $< 10^7$ ohm cm resistivity is reached when pyrolyzed to 700°C).

Measurements in Paramagnetic resonance absorption (*Figure 2* and *Figure 3*) show that the concentration of unpaired electrons increases steadily to approximately 600°C. and then falls rapidly above that temperature. The mechanism for the pyrolysis of this type of material as suggested by Dr. Baker is shown in *Figure 2*. His experiments indicate that as the pyrolysis continues above

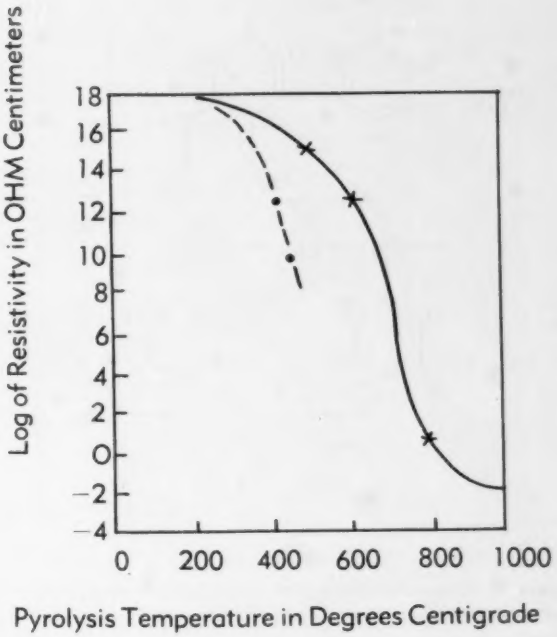
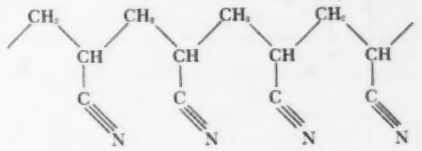
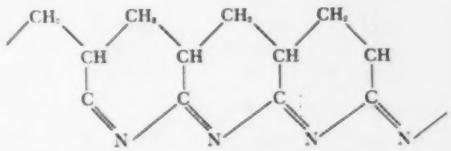


Figure 1. Specific resistivity of (a) pre-oxidized polydivinylbenzene pyrolysates and (b) polyvinylidene chloride pyrolysates at about 25°

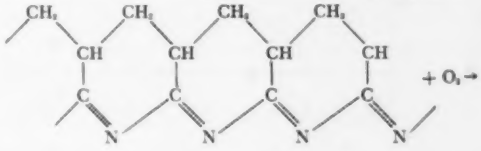
700°C, the aliphatic carbon, the hydrogen and the oxygen atoms are split up and the resultant material approaches a graphitic structure containing only carbon.

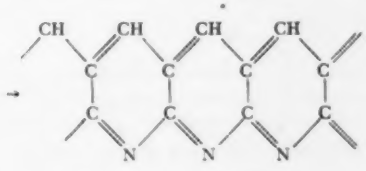
It is also of considerable interest to note the results obtained from the study of the products of the thermal conversion of polyacrylonitrile. It is believed that during thermal treatment polyacrylonitrile undergoes the following conversion (8, 9):





AND then owing to dehydrogenation by oxygen





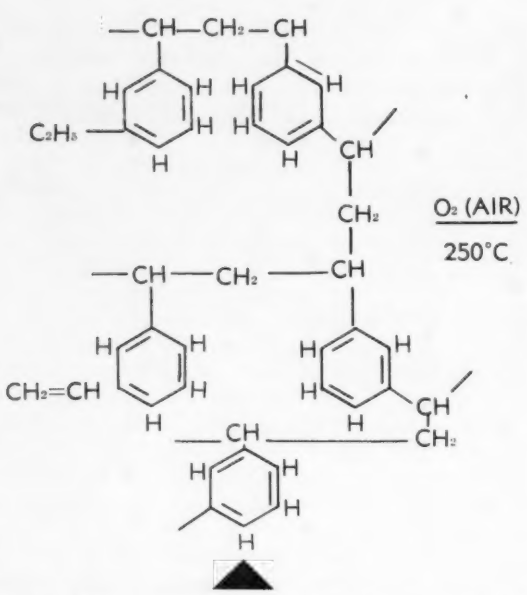


Figure 2. Schematic conversion of divinyl benzene/ethyl vinyl benzene copolymer to a carbon-like semi-conductor (See P. H. Winslow et al)

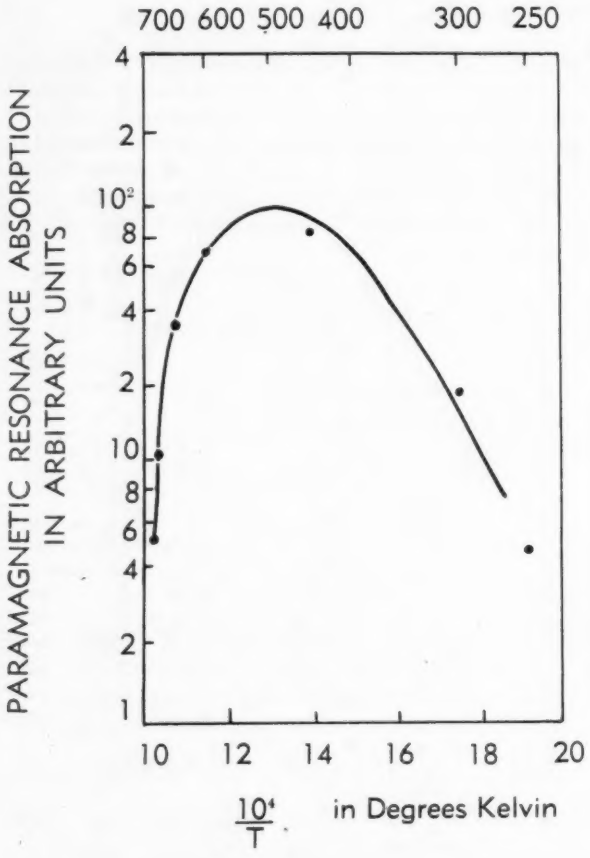
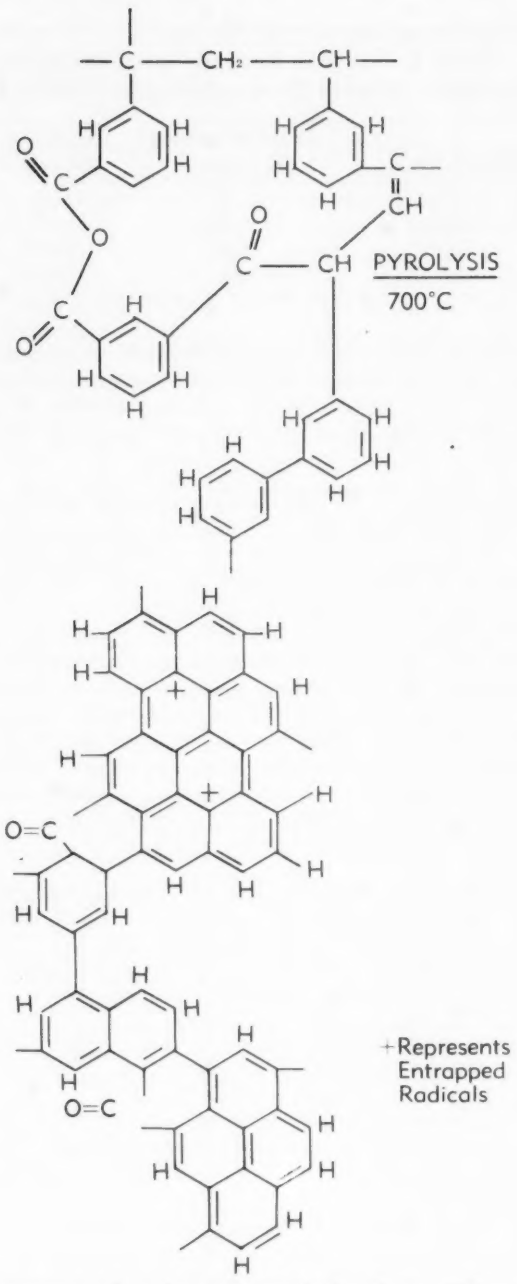


Figure 3. Paramagnetic resonance absorption in preoxidized polydivinylbenzene as a function of progressively higher temperatures of pyrolysis. (Reprinted with permission of the Editor, J. Pol. Sci., **16,** 101, 1955)



The presence of conjugated double bonds as well as regularly alternating nitrogen atoms, having a pair of electrons which do not form a chemical bond and which are under the action of both the vinyl (with reference to the nitrogen atom) and the alkyl bond, leads to expect semiconductor properties for these polymers.

An investigation was made (12) of semi-conductor properties of the products of thermal conversion of polyacrylonitrile prepared in the presence of: 1. organometallic catalysts (Butyl lithium at low temperature-Molecular weight 10.000); 2. lithium in liquid ammonia by redox initiation (Molecular weight 100.000); 3. polymer obtained by ionic polymerization, with subsequent irradiation by a dose of γ radiation.

The thermal treatment of polyacrylonitrile was carried out:

a. in a vacuum, with evacuation of the escaping gases
b. in a previously evacuated autoclave
c. in air, with subsequent heating up to 400-500°C
d. in a vacuum and also under ammonia pressure

Using the capacity of polyacrylonitrile to swell in solutions of inorganic salts, samples of the products of thermal conversion of this polymer were prepared containing 2-3% iron, copper and chromium salts.

The samples obtained were investigated with the help of EPR. All measurements of the EPR spectra (*Table 3*) were carried out at room temperature. Dependence of electrical conductivity on temperature was determined too. The results of measuring the dependence of the specific electrical conductivity on temperature, the thermoelectric power and the calculated activation energy are given in *Figure 4 and Table 3*.

These data show that all the substances obtained possess p-type conductivity (thermoelectric power positive). The values of the activation energy lie in the range of 0.65-0.32 ev. The specific electrical conductivity at 20°C for the sample cited is in the range of 10^{-10} -10^{-15} ohm^{-1} cm^{-1}. Thus, the activation energy, the electrical conductivity and the thermoelectric power that was obtained for the polymeric substance have an order of magnitude customary for semi-conductors. Thermal treatment of polyacrylonitrile under ammonia pressure leads to a considerable increase in electrical conductivity. Moreover, with the introduction of the metallic salts, the activation energy is noticeably reduced.

Polymers with Metallo-cyclics in the chain of conjugation

Interesting results have been achieved in the last 2-3 years in the area of synthesis of polymeric compounds containing metallocyclic (chelate) groups (13). Of these polymers phtalocyamines possess the highest thermal

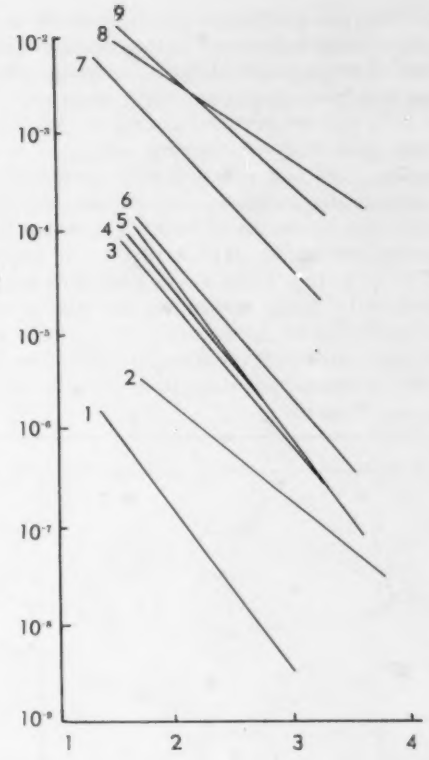


Figure 4. Dependence of Electrical Conductivity on Temperature

$$G = f\left(\frac{1}{T}\right)$$

NOTE: Indexes of the Curves Correspond to the Sample Numbers in the Table 2.

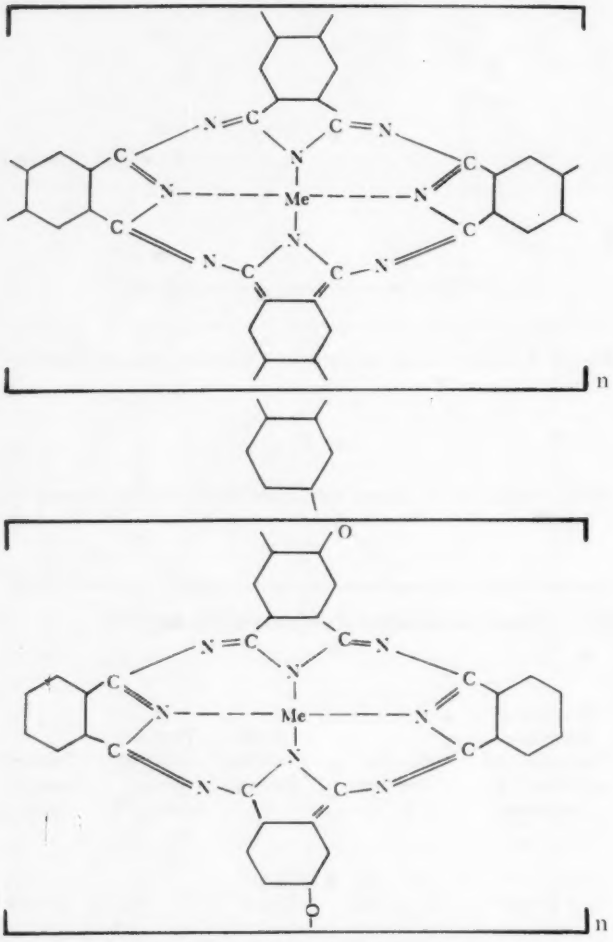
Table 3. Electrical and Paramagnetic Properties of Semi-conductor Polymeric Materials

Sample No.	Polymer and Method of Production	Treatment: Thermal °C	Treatment: Chemical	Number of Electrons with unpaired spins in 1 g of material	G, ohm^{-1} cm^{-1} at 20°C	Activation Energy, ev	Thermoelectric power, in mv/°C	Type of Conductivity
1	PAN*, redox polymerization	400	—	2.0×10^{19}	2×10^{-9}	0.64	—	—
3	The same	400	In NH_3 presence	2.6×10^{19}	2×10^{-7}	0.64	+75	p-type
5	The same	500	Same	2.0×10^{19}	2×10^{-7}	0.64	+108	same
7	The same	500	$CuCl_2$	1.5×10^{19}	1×10^{-5}	0.51	+72	same
4	Polycondensate of phthalic anhydride with hydroquinone	250	—	5.9×10^{19}	7×10^{-7}	0.58	—	same
6	Polycondensate of phthalic anhydride with hydroquinone and glycerine	250	—	7.8×10^{19}	2×10^{-7}	0.85	—	—
2	Polyvinylchloride	25-	—	2.2×10^{17}	7×10^{-9}	0.4	—	—
9	Fabric made of PAN #1	500	—	—	2×10^{-4}	0.43	+110	p-type
8	Fabric made of PAN #2	500	—	—	3×10^{-8}	0.32	+81	same

1. PAN = Polyacrylonitrile
2. Sample numbers correspond to indexes of curves in the figure.

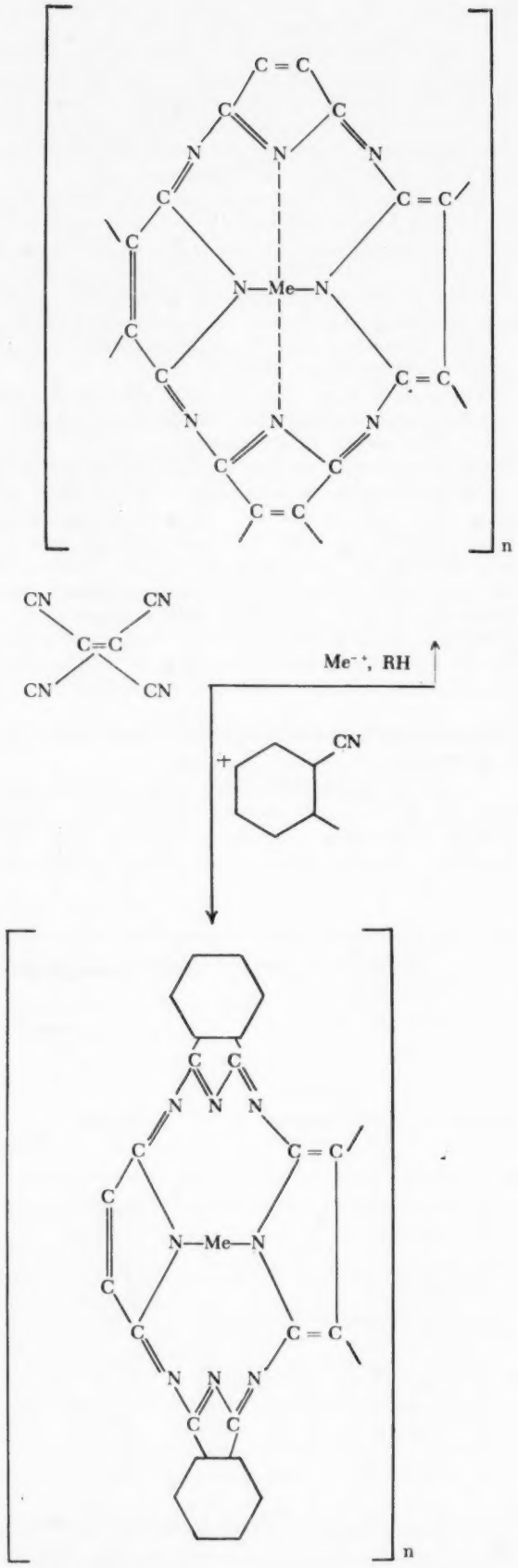
stability. These are substances in which an atom of metal is bound to nitrogen atoms in heterocyclic system in the basic chain of conjugation of the macromolecule.

Polymers of phthalocyanine were obtained by interaction of 3,3′, 4,4′-tetracyanodiphenyl or 1,2,4,5-tetracyanobenzene with salts of copper, iron, and a series of other metals, (14), on reaction with pyromellitic acid, phthalic anhydride, and urea and copper salt at 170 to 200°C, and also by means of melting together 3,3′, 4,4′-tetracyanodiphenyloxide, phthalonitrile, and copper chloride at 275° (14, 15). Polymers of phthalocyanine which are formed under these conditions are partly soluble in dimethylforamide with formation of nonviscous solutions. Such polymers withstand heating to 350°. On the basis of their IR spectroscopic data it is possible to develop the following structure:



Investigation of the electrophysical properties of polyphthalocyanines based on 1,2,4,5-tetracyanobenzene and copper showed that these substances are typical semiconductors with an activation energy for conduction of 0.26 ev, and P293 = 40 ohm cm, and a concentration of current carriers of 10^{18} to 10^{14} in 1 cm at 20°.

Not long ago, a new type of polymeric chelate compounds containing basically carbon, nitrogen, and metals was synthesized (16, 17). These polymers are obtained by the interaction of tetracyanoethylene or its mixture with phthalonitrile with metals or their compounds at 160 to 300°C and are depicted at right.



This work showed the possibility of carrying out the reaction of polycoordination directly on the surfaces of metallic objects through their treatment with vapors of percyanoethylene or its mixtures with aromatic di or polynitriles. As a result of such treatment, the metal is covered by a surface film of polymeric chelate complex, securely bonded to it by chemical bonds.

Also, the means was developed for obtaining plastics upon compression or mixtures of finely ground metals, metallic salts, or oxides with percyanoethylene or its mixtures with aromatic di or polynitriles (17). Polymeric chelate complexes of percyanoethylene are crystalline, chemically stable, do not burn, and resist heating for a long time without destruction at 500°C. Crystallinity in polymers of percyanoethylene is attained only when polycoordination is accomplished on the metal reagent interface. On conducting the reaction of percyanoethylene with metal acetylacetonates in solution, that is, in homogeneous condition, polymeric substances are formed which do not show crystallinity.

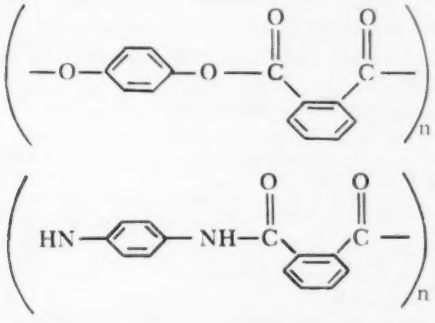
Evidently in this case, regularity of polymer structure is determined by the crystallinity of the metal and by orientation of the reagent molecules in the adsorbed layer on the interface.

Polymeric complexes of percyanoethylene are characterized by high values of dielectric constant and magnetic susceptibility ($x = 0.6 \times 10^{-4}$) and possess properties of semi-conducting materials. The activation energy of electroconductivity of such polymers is 0.21 to 0.26 ev at $\gamma = 10^{2}$ ohm^{-1} cm^{-1} (18).

Polymers Containing Hetero-atoms

There are also a number of papers (7, 10, 12) on polymers with conjugated double bonds containing hetero-atoms in the principal chain.

From this point of view there is an interest in the products of the polycondensation of phthalic anhydride with hydroquinone and n-phenylene diamine having the following hypothetical structure:

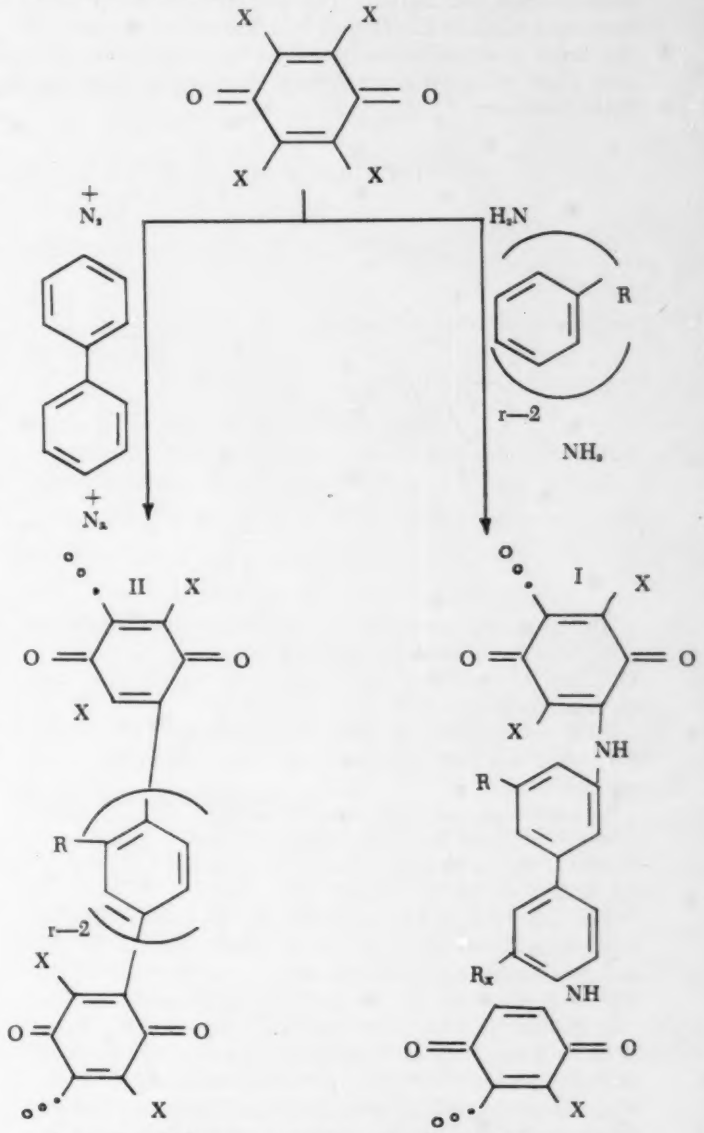


The hypothetical structure of both polymers leads us to expect the appearance of semiconductor properties, in view of the conjugated double bonds alternating with unpaired valence electrons of oxygen and nitrogen. The paramagnetic and electrical properties of the designated polymers are given in *Table 3 and Figure 4* (curves 5 and 6).

For the purpose of obtaining a three-dimensional polymer by the polycondensation of phthalic anhydride with hydroquinone, glycerine was introduced into the reaction mixture, but the crosslinks produced did not appear to have a noticeable effect on the electrical properties.

Of great theoretical and practical interest was the recent synthesis of a polymeric aromatic compound containing quinone and amino groups in the chain of conjugation (19).

Such polymers were obtained by interaction of chloranil with 4,4-diaminodiphenyl and its derivatives, and also by reaction of benzoquinone with aromatic diamines bis-diazo benzidine.



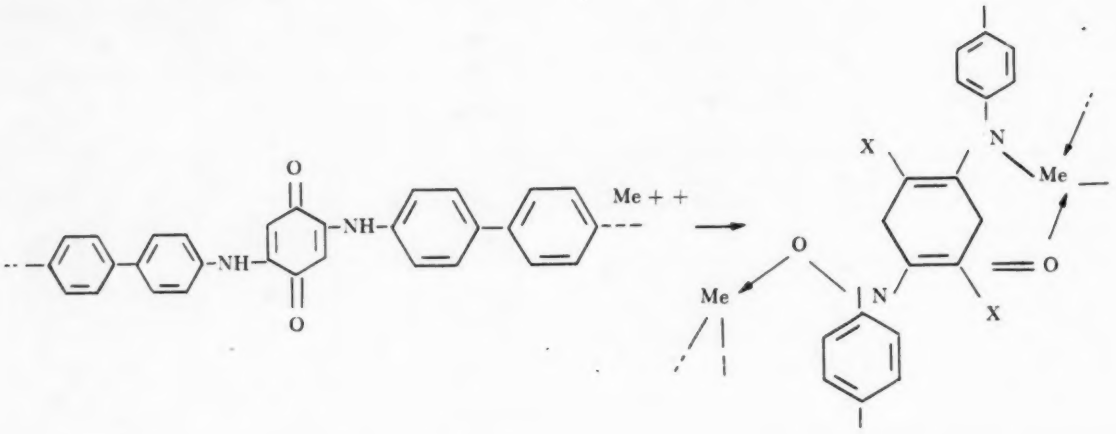
where X is halogen or H; R is H, alkyl, COOH, etc.

The presence of active atoms of chlorine and other functional groups (R) in polyphenyleneaminoquinones (I) and polyphenylenequinones (II) opens practically unlimited possibilities for modification of properties and synthesis of various polymer analogs.

Polyphenyleneaminoquinones are characterized by relatively high values of the magnetic susceptibility constant ($X = 1{,}28 \times 10^{-6}$) and by its relationship to the magnetic field strength (X decreases with increasing field strength).

Aromatic polyphenylaminoquinones, in contrast with aliphatics, show narrow electron paramagnetic resonance (EPR) lines of high intensity with G-factors of free electrons. Besides narrow lines, there is wide line EPR with an interval between maxima of 500 to 600 ersteds which corresponds to 10^{21} to 10^{23} unpaired electrons per gram for paramagnetics.

The EPR spectra of such compounds strongly resembles spectra of nucleic acids and their complexes with proteins observed earlier. The presence in polyphenylaminoquinones of C=O and NH groups substituted in the ortho position makes possible the preparation of a new class of polymeric chelate compounds based on these polymers.



The magnetic susceptibility constant of the complex of polyphenyleneaminoquinone with copper is X = 3.7 x 10^{-6}, and it decreases with increasing temperature and magnetic field strength.

EPR investigation of these complexes shows wide assymetrical lines of high intensity with absorption in a neutral field.

Investigation of electroconductivity of polyaminoquinones showed that, for polymers of type 1 (with R = COOH), the activation energy for conduction is E = 0.5 to 60.6 ev for $\sigma_o = 210^{-3}$ ohm^{-1} cm^{-1}.

The specific magnetic and electrical properties of polyphenylaminoquinones (1) are evidently caused by the ease of forming semiquinone radicals by the fate of the unshared electrons of nitrogen in the general chain of conjugation, and by formation of intermolecular structures with the help of hydrogen or chelate bonds. Such polymers possess catalytic activity in reactions of oxidation, reduction, and, in part, are highly effective heterogeneous catalysts for hydrogen peroxide dissociation.

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Dynamic Measurement of Mechanical Moduli I.

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Equipment for Automatic Recording of Shear & Flexural Amplitude-Time Curves in Free Vibration

Both Young's and shear moduli can now be measured on the identical sample by a free vibration method. In the glass transition range Poisson's ratio dips. In the rubbery region values above the infinitesimal strain limit of 0.5 are noticed.

Most of the measurements of mechanical moduli of polymers have involved independent determination of the shear or Young's modulus only. Apparatus designed to measure one is not necessarily well suited to the measurement of the other. In particular it is not easy to make measurements of both shear and Young's modulus on the same identical sample. Yet, both measurements are necessary for a complete description of mechanical properties in the infinitesimal strain approximation. Bulk modulus and Poisson's ratio may be calculated.

The literature reports few data on Poisson's ratio for polymers. Takei (1) reports Poisson's ratio for rubber. Kono (2) reports high-frequency measurements for polystyrene and polymethylmethacrylate and Kaguk (3) reports high frequency measurements for polyethylene. Smith (4) has studied Poisson's ratio of filled poly(vinyl acetate) using static techniques. In no case do the data extend past the glass transition temperature. Since Poisson's ratio lumps shear and stretching effects into one parameter, this quantity was determined here.

This article describes equipment for automatic recording of time-amplitude curves in free-vibration experiments by means of a transducer and a recorder. By using cylindrical rods as torsional and flexural pendulums, both shear and Young's modulus may be calculated for the same specimen. This eliminates sample-to-sample variation, but effects due to temperature-cycling remain. Young's modulus and damping, shear modulus and damping, and calculated Poisson's ratios are reported for polypropylene, Nylon 66 and poly(methylmethacrylate).

The Flexural Pendulum

A massless rod can be considered to be suspended vertically with a weight on the free end. If the rod is bent by a force on the end, the elastic restoring force is

$$F_1 = 3ECy/l^3 \qquad (1)$$

where E = Young's modulus, C = moment of area of the rod around the neutral axis ($C = \pi r^4/4$ for a circular cylinder), y = the displacement of the end of the rod from the neutral position and l = length of rod.

In addition, there is a gravitational restoring force, for small displacement, of

$$F_2 = mgy/l \qquad (2)$$

where m = mass of suspended weight.

Assuming damped Hookean behavior, the differential equation of the flexural pendulum is

$$my'' + Ry' + [(3EC/l^3) + (mg/l)]\, y = 0 \qquad (3)$$

It follows from the solution of (3) that

$$\Phi = 4\pi^2\nu^2 + 2m/R = (3EC/ml^3) + (g/l) \qquad (4)$$

where ν = natural frequency of pendulum. A plot of Φ versus l/m for different masses gave experimental straight lines from whose intercepts a good value for the acceleration of gravity could be read. The analysis of the torsional pendulum was given by McLachlan (5).

Experimental Procedure

Torsional and flexural pendulums were designed and built employing Statham resistance-wire strain gauges as sensing elements. General schematics of these instruments are shown in *Figure 1*. In both cases, typical frequency and amplitude decay curves were obtained by recording the reaction of the strain gauge on the chart of a Sanborn Series 150 oscillographic recorder. The frequency and logarithmic decrement, α, were determined from the resulting plots.

Torsional vibrations were manually induced (by straining the sample rod torsionally through a 90° arc and then releasing) in all cases except the nylon. Here, the apparatus was fitted with a lever mechanism whereby the torsion head assembly could be rapidly swung through an arc of 45° and abruptly stopped. A torsional vibration was thereby induced into the specimen by reactance. This enabled the nylon (6) to be activated while in a controlled dry atmosphere.

The flexural experiments were carried out in a completely enclosed 3000 ml. glass resin flask with dessicant present to maintain low humidity conditions. The vibrations were manually induced by shaking the unit along a plane parallel to the direction of sensitivity of the strain

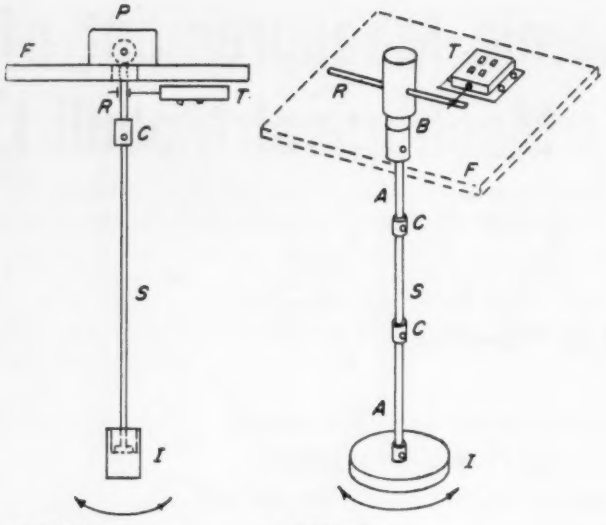

Figure 1. Schematic diagram of apparatus

A—Steel Adapter Rod
B—Bearing
C—Clamp
F—Frame Support Plate
P—Pivot Bearing Assembly
R—Torque Rod
S—Test Specimen
T—Statham Transducer
I—Inertial Mass

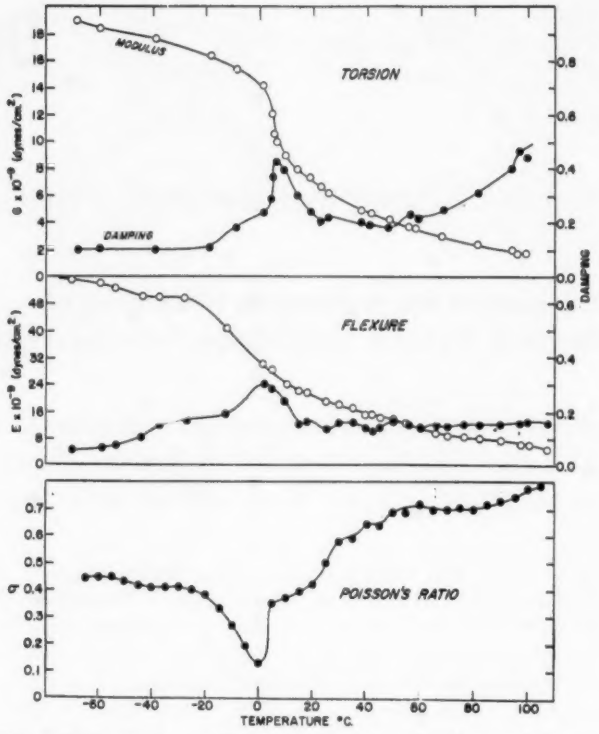

Figure 2. Dynamic mechanical properties of polypropylene

gauge. With both these instruments, the test frequencies were held between 2 and 6 cps. by changing the torsion disk or mass setting the course of the freely vibrating system. The masses were designed so that their centers were focused at the lower end of the rod.

Temperature control was to within ± 0.5°C. in these experiments. Above room temperature, a circulating air heating jacket was employed and below room temperature, ice water, dry ice-acetone and liquid nitrogen baths were used. The temperature was read from a thermocouple situated adjacent to the polymer rod. Elongation of the sample due to the weight of the inertial mass was negligible at all temperatures except near the melting temperature of the polymer, above which no measurements were obtained. Specimens were 3/32" to 1/8" diameter and 5" long.

Samples of poly(methylmethacrylate) and Nylon 66 were obtained as rods from Polypenco Corporation. The Polypropylene rod was an extrusion of Hercules Profax Polypropylene. The samples were placed in a rotating clamp arrangement and machined to a circular cross-section with carborundum paper. They were tested for uniformity with a caliper before use. Each sample was annealed for at least 3 hours 10° to 30° below its flow temperature before any measurements were made. Torsional and flexural data were obtained successively on the same specimen to minimize variations.

Dynamic Mechanical Data

In *Figures 2, 3 and 4* are shown the dynamic mechanical data obtained on polypropylene, Nylon 66 and poly(methylmethacrylate). These data may be compared with results given by other authors (7, 8, 9). Typical damping peaks were obtained for polypropylene and Nylon 66 at the glass transition temperatures, (T_g). Of particular interest is the observation that T_g determined torsionally is slightly higher than that obtained flexurally (*Table I*). This suggests that different relaxation mechanisms may be operative under these two types of deformation. A comparison of the torsional and flexural data for Nylon 66 shows large differences especially in the damping curves. The flexural data resemble the behavior of Nylon 66 in the presence of small amounts of water (*see Figure 1*, reference 6). However, precautions were taken to exclude moisture in all our measurements on this polymer and it is unlikely that moisture is responsible for the observed results. It may also be pointed out that the flexural damping curve for polypropylene is somewhat surpressed compared to the torsional case. The data obtained on amorphous poly(methylmethacrylate) were not clear-cut, but reflected typical behavior.

Poisson's Ratio

Using the measured shear and elastic moduli, Poisson's ratio was calculated from the equation, $\sigma = (E/2G) - 1$, through the temperature range and several unexpected results were obtained. At the transition region, a sharp dip in σ was observed. This is probably caused by the shift in observed T_g between torsionally and flexurally determined moduli. Since G starts to decrease at a higher temperature than E, the variation in σ would result in a dip at the transition region. Furthermore the location of this dip occurs at a temperature range intermediate between the glass transition temperatures.

It is of potentially broader significance that for the three polymers studied, a temperature region is reached where σ becomes greater than 0.5. Such behavior indicates a volume decrease when the polymer undergoes logitudinal stress. It is observed that these regions occur

Table 1. Transition Temperature of Various Polymers

	Torsional	Flexural	Poisson's Ratio
Polypropylene	6° to 9°C.	−2 to +2°C.	0° to 5°C.
Nylon, T_g	80° to 90°	65° to 75°	70° to 80°C.
minor	−115° to −105°	−120° to −140°	—
Poly(methylmethacrylate) (12)	115°	105° to 115°	—

near the glass transition range, where the values of E and G are lowest. The experimental errors would thus be magnified in this range and could account for this unusual result, especially for Nylon 66 and poly(methyl methacrylate). However, Poisson's ratio values in excess of the infinitesimal strain limit 0.5 have been observed in rubbers, where volume decreases on stretching have been attributed to a phase change (microscopic crystallization) during deformation (10). The fact that three diverse polymers have Poisson's ratio values that behave anomalously in the same region speaks against this behavior being an artifact. Further verifications must be ascribed to failure of the system to obey the infinitesimal-strain classical theory of elasticity (11).

The negative values of Poisson's ratio calculated above 110° for poly(methylmethacrylate) are based on measurements made in a region of incipient flow. Since the shear and Young's moduli approached each other in value in this region, resistance to deformation may be becoming independent of direction here.

Acknowledgment

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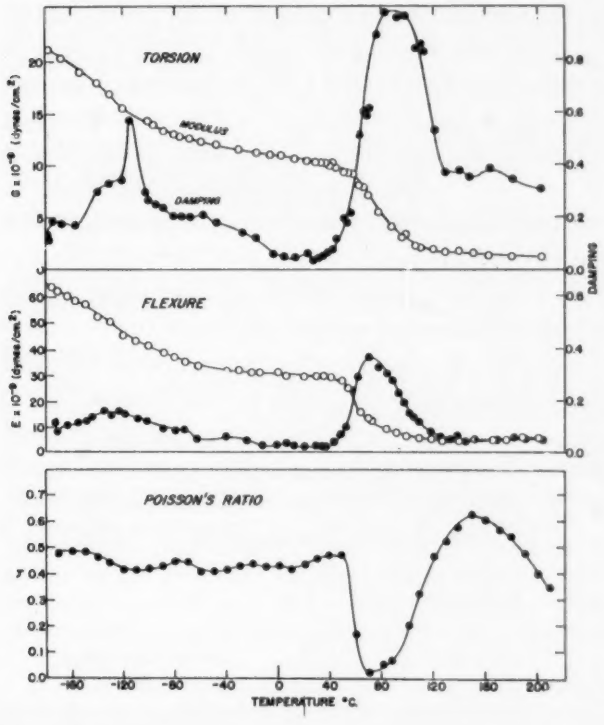

Figure 3. Dynamic mechanical properties of nylon 66

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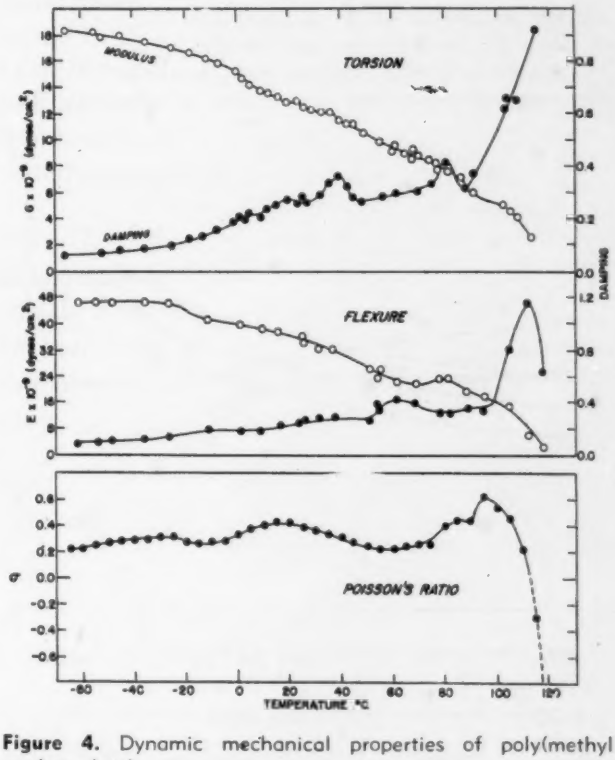

Figure 4. Dynamic mechanical properties of poly(methyl methacrylate)

An Introduction to the

GLASS-RESIN INTERFACE

Section

With a view to recording more of the basic glass-resin interface data into the permanent literature, SPE TRANSACTIONS has undertaken to publish the articles which appear on the following pages. Five of these papers were originally presented at the 16th Annual Technical and Management Conference, Reinforced Plastics Division, Society of the Plastics Industry, Edgewater Beach Hotel, Chicago, Illinois. The article entitled: "The Degree of Bonding Between Coupling Agents and Glass Filaments," was not presented at this meeting, but at the Continuous Filament Winding Symposium of the Society of Aerospace Material and Process Engineers, Pasadena, California, March, 1961.

The first group of articles are studies of chemistry and surface phenomena involved in the glass-resin interface. Effects of different types of glasses and glass surfaces, resin systems and coupling agents are studied in order to help advance the understanding of the reactions and mechanisms involved here, as well as their influence on physical properties of the laminate. Methods for the study of these properties are also presented.

The last paper uses some techniques developed in the first group to study the strength and nature of the interfacial bond, helping to integrate the data of the seminar.

Physical Techniques Used in Studying Interfacial Phenomena

Classical surface chemistry methods can be used to investigate glass-resin interfacial interaction. Increased knowledge of the fundamentals will lessen the empirical nature of glass-reinforced resin research

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In many areas of research there are fundamental requirements which are already established, making the work of the investigator one of applying the fundamentals to the areas in question. In the area of glass-reinforced resin research there are few fundamentals which are available to the investigator and the effort becomes quite empirical in nature. It is necessary to determine the fundamental principles of glass-resin interaction in order to bring a better understanding to the current "art".

There are two main factors which must be considered before a glass-resin system is completely defined:

1. The interfacial glass-polymer bond
2. The cohesive bonds in the bulk of the glass and the resin.

This paper will place the emphasis on interfacial bonds, as distinct from the internal, or cohesive, bonds.

The Interface

In considering interfacial phenomena it is well to define precisely what is meant by an interface. When two incompatible materials are brought together, an interface is generated. There are liquid-liquid, liquid-gas, liquid-solid, gas-solid, and solid-solid interfaces. There is a tendency to consider an interface as a sharp line of demarkation. Doubtlessly, the interface is a zone due to mixing of the substrate and superstrate. *Figure 1* schematically presents the probable interrelationship existing at an interfacial zone when an organic liquid is placed on a metal substrate.

It is generally felt that a discussion of interfacial phenomena is concerned with the zone a few microns on either side of the imaginary line which would be the interface. For the sake of convenience, the report presented here will take advantage of this approach.

The literature associated with investigations of interfacial phenomena is voluminous. In this general discussion, only certain key references will be included.

As the glass-resin bond is of the interfacial species, surface chemical phenomena are involved. In order to study this general area, surface chemical techniques, with emphasis on adsorption, are obviously necessary.

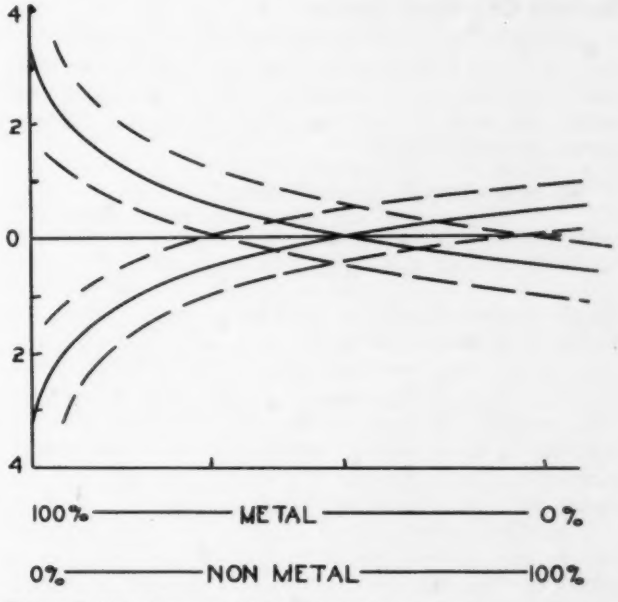

Figure 1. Metal-non metal interfacial interaction

Table 1. Surface Energy of Monolayers of Organic Materials

Surface Component	Surface Energy (γ_c) in Dynes
—CF_3—terminal	6
—CF_2H—terminal	15
—CF_2—in chain	18
—CH_3—terminal	22
—CH_2—in chain	31
—CH= —benzene ring on edge	35
—C(Cl)(Cl)— vinylidene chloride	43

In reviewing the literature, one is struck by the fact that much adsorption work has been reported, but mainly on powdered substrates (1-9). The very form of the substrate allows only one variable to be determined; namely, the weight change which is evidenced during adsorption. It has been found that it is not necessary to work with powdered metal, or glass, substrates. Although plane surfaces will not adsorb a weighable film, the adsorption may be readily measured by other methods. Techniques which may be utilized include:

1. The transfer of mono- and multilayers by means of an automatic film balance
2. The examination of surfaces in an ellipsometer
3. The determination of contact angles by means of a contact angle goniometer
4. Radiotracer counting of samples coated with ultrathin films of the material in question
5. The determination of surface potentials
6. The examination of adsorbed films by elegant infrared techniques
7. Dynamic desorption from planar surfaces
8. The use of electron and x-ray diffraction

Surface Chemistry Review

Adsorption at a surface from solution is considered to be due to the differences in potential energy of surfaces and the molecules in solution. Surface energy is generally the product of an intensity factor and a capacity factor, or more simply:

$S = \gamma s$ where S = surface energy
γ = surface or interfacial tension in ergs/cm.^{2}
s = surface area in cm.^{2}

As all systems attempt to reach lower energy states, the tendency to reduce the surface area will reduce the surface energy; viz., two drops of mercury coalescing. Pure liquids reduce surface energy by reducing the surface area; solutions by reducing the surface tension. The adsorption of many organic materials onto a high energy surface markedly reduces the surface energy and the newly formed surfaces are then low energy in nature.

Typically, monolayers of organic materials adsorbed on chrome surfaces result in the surface energies as shown in *Table 1* (9). (γ_c refers to the critical surface energy.)

Contact Angle and Surface Energy

It is possible to determine γ_c, or the critical surface tension, at the solid-liquid interface (γ_{s1}) by the Freundlich equation (10) which takes advantage of the changes in solubility due to particle size.

$$\gamma_{s1} = \frac{RTDr}{2M} \ln \frac{C_2}{C_1}$$

Where

R = gas constant = 8.31 x 10^7 ergs
T = °K
D = density, solid phase
r = radius of the solid particles
C_2 = concentration of solution in equilibrium with the particles of radius r
C_1 = concentration of solution in equilibrium with the larger particles (massive solid phase)
γ_{s1} = interfacial tension of the solid-liquid = γ_c
M = molecular weight of substance being determined

A very convenient method for obtaining the critical surface tension is by determining the contact angle, *Figure 2*. The contact angle θ between a liquid and a solid ranges from complete wetting (0°) to complete non-wetting (180°). Actually, angles greater than 110° seldom exist. Further contamination of the surface by an air or water surface reduces the interfacial energy γ_{sg}, by an amount π_e (11) and accordingly the Young equation (12) appears as:

$$\gamma_{sg} - \pi_e = \gamma_{s1} + \gamma_{1g} \cos \theta \qquad (1)$$

The interfacial energy is numerically equal to interfacial tension. Interfacial energy has the dimensions of erg/cm.^{2}, while interfacial tension has the dimensions dynes/cm.

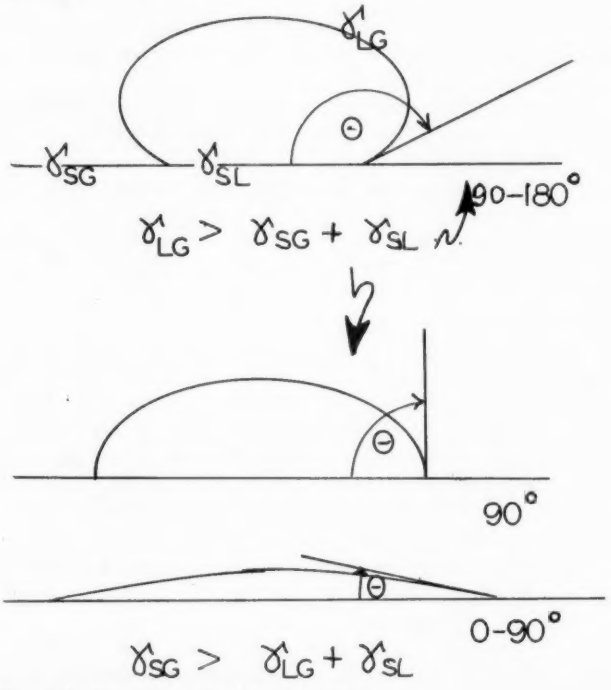

Figure 2. Contact angle determination

Dupre suggested that W_A, the reversible work of adhesion of liquid and solid is as follows:

a) with a clean adhesive break

$$W_A = \gamma_{sg} + \gamma_{lg} - \gamma_{sl} \quad (2)$$

b) with material remaining

$$W_A = \gamma_{sg} - \pi_e + \gamma_{lg} - \gamma_{sl} \quad (3)$$

The work of adhesion should not be confused with the strength of adhesion. Combining equations (1), (2) and (3) one obtains:

$$W_A = \pi_e + \gamma_{lg}\,(1 + \cos\theta) \quad (4)$$

and

$$W_A = \gamma_{lg}\,(1 + \cos\theta) \quad (5)$$

If the adsorbed layer has the same properties as the liquid, complete wetting occurs and $\theta = 0$. $W_A = W_C$, the work of cohesion, and (5) becomes:

$$W_C = 2\,\gamma_{lg} \quad (6)$$

The surface energy ϵ of a substance, differing from the free surface energy, is defined by the relationship:

$$\epsilon = \gamma - T\frac{d\gamma}{dT} \quad (7)$$

$\frac{d\gamma}{dT}$ is generally a negative quantity, and is equal to the change in surface entropy. When 1 cm.^{2} of surface is created isothermally, the work γ has to be supplied, plus the heat of $-\,T\frac{d\gamma}{dT}$.

General Thermodynamics of Spreading

Oil will spread on water if cohesion is less than adhesion. In the case of films greater than a monolayer, duplex spreading may occur. Duplex spreading forms a film greater than a monolayer with complete independence between the surface energy of its outer surface and that of the interface with the phase on which it is spread. These films tend to be unstable and separate to a lens and monolayer equilibrium. The spreading coefficient

$$S_{\underset{a}{b}} = W_A - W_C \quad (8)$$

but

$$W_A = \gamma_{sg} + \gamma_{lg} - \gamma_{sl}$$

and

$$W_C = 2\,\gamma_{lg}$$

then

$$S_{\underset{a}{b}} = \gamma_{sg} + \gamma_{lg} - \gamma_{sl} - 2\,\gamma_{lg} = \gamma_{sg} - (\gamma_{lg} + \gamma_{sl}) \quad (9)$$

Oil will spread as a duplex film if the surface energy of the disappearing surface, γ_{sg}, is greater than the sum of the energies of the two new surfaces formed, or:

if $S_{\underset{a}{b}}$ is positive, duplex spreading will occur.

if $S_{\underset{a}{b}}$ is negative, duplex spreading will not occur.

Adsorption

Those substances which tend to reduce the surface energy, tend to concentrate at a liquid-vapor interface. Those substances which lower the interfacial energy tend to concentrate at a liquid-solid or liquid-liquid interface.

Freundlich (10) developed the following equation which has no limit to the number of adsorbed layers:

$$x = aC^b \text{ or } \log\frac{x}{m} = \log a + b\log C$$

where

x = wt. adsorbate (gm.) C = conc. of soln. at equilibrium
m = wt. adsorbent (gm.) a and b = consts.

Langmuir (13) considered only monolayers. Once the active centers are filled up, there is no further adsorption.

$$X = \frac{\alpha\beta C}{1 + \alpha C}$$

where

X = weight of adsorbate
C = equilibrium concentration
α,β = constants

Brunauer, Emmett and Teller (1) developed a classical equation defining polylayer adsorption. They considered the rates of evaporation of the adsorbate molecules from, and condensation onto, a surface in both mono- and possibly polymolecular layers.

$$\frac{P}{V(P_o - P)} = \frac{1}{sVm}\,\frac{(s-1)P}{sVmP_o}$$

where

V = volume gas adsorbed at pressure P
V_m = volume gas to just complete a unimolecular layer on the surface
P_o = liquefaction pressure of gas (T° of observation)
s = constant

$$s = e^{-\frac{E_a - E_1}{RT}}$$

where

E_a = heat of adsorption of the first layer
E_1 = heat of adsorption of the successive layers, approximately the heat of liquefaction of gas.

Harkins and Jura (14) differentiated between the free energy and the total energy of a surface. For example, at 20°C, in a water system:

Free surface energy = surface tension = 72.8 ergs/cm.^{2}

The total energy, $h = \gamma - T\left(\frac{d\gamma}{dT}\right) = \gamma + I$

where

I = latent heat of a surface = 45.7 ergs/cm.
then h becomes 72.8 + 45.7 = 118.5 ergs/cm.^{2}

Adsorption of Polymers

Adsorption is accompanied by increased orderliness and, therefore, by a more negative entropy. In simple

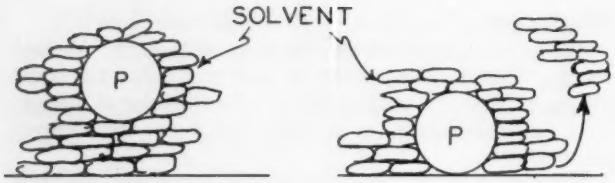

Figure 3. Schematic representation—polymer molecule approaching and adsorbing on a surface

systems, it is not too difficult to appreciate the mechanism of adsorption of condensed layers on to a surface. One can understand the molecules of the adsorbate, e.g., stearic acid, approaching a high energy surface; becoming attached to the surface, satisfying active centers on the surface, by either reacting to form chemical bonds, or by simply approximating the surface and forming physical bonds; and lastly by forming a condensed oriented film reducing the surface tension to a marked degree and, therefore, causing a more negative entropy. However, the adsorption of more complex molecules onto a surface is not as readily explained.

In considering a polymer in solution randomly approaching a surface, a two phase system results. The portion of the molecule which is adsorbed onto the surface differs substantially from the portion remaining in solution. *Figure 3* schematically represents a polymer molecule, which is completely solvated, approaching a surface. Work must be done to displace the solvent molecules on the surface and additional work is necessary to adsorb the polymer. The polymer molecule is then solvated only on the upper areas and is, essentially, not in solution where it is attached to the substrate. The solvating power of the solvent is of considerable importance.

A very good solvent allows the polymer to become quite swollen and well surrounded by solvent as is shown in *Figure 4a*. *Figure 4b* indicates the polymer in a poor solvent, showing the compressed nature of the polymer molecule, thus allowing for a greater concentration of polymer on a given surface. Some workers feel that the poor solvent precipitates the polymer out faster than a good solvent. It is this writer's opinion that the greater concentration at the surface is due to the fact that the more tightly balled polymer is able to pack more readily than the satiated more soluble specie. As weight increase has, in general, been the method by which adsorption has been measured, no packing information is available.

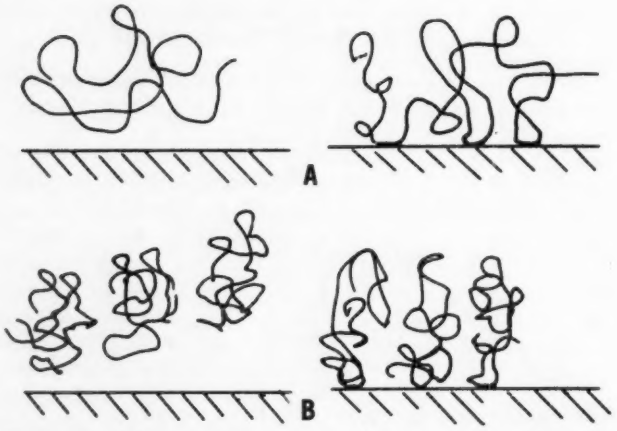

Figure 4. Polymer adsorption: a. from a good solvent; b. from a poor solvent

F. Eirich (15) has summarized the variables which are important in polymer adsorption. They are listed below:

1. Polymer: type; chemistry; shape and flexibility.
2. Solvent: chemical attraction for polymer and surface; dielectric constant.
3. Adsorbent: surface energy; chemistry of surface; geometry of surface.
4. Molecular weight and molecular weight distribution.
5. Active substituents on polymer.
6. Temperature: generally will decrease adsorption; however, with polymers, may well cause increased adsorption.
7. Reversibility.
8. Effect of impurities.

A typical adsorption isotherm which may be prepared from adsorption data is shown in *Figure 5*.

Polymers have been shown to fit the adsorption isotherm of Langmuir, although this equation was developed for gaseous monolayers.

Orientation

When a drop of an anisotropic liquid is placed on an active surface, orientation occurs at the solid-liquid interface, *Figure 6*. At the same time, orientation occurs at the liquid-gas interface. The molecules will align themselves in a manner which is dependent on the material. For instance, ethyl alcohol will align as shown in *Figure 6*. The rod represents the alkyl chain, and the ball the OH group.

In addition, let us examine a benzene-water system, *Figure 7*, in which the benzene contains dissolved stearic acid. At the interface there will occur a layer of oriented stearic acid molecules which orient with the alkyl chains

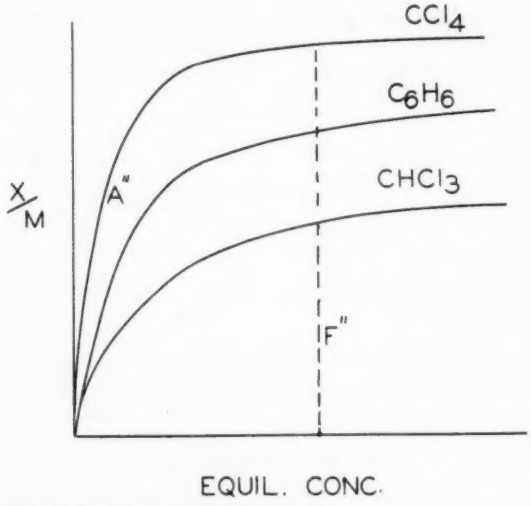

Figure 5. Typical adsorption isotherms

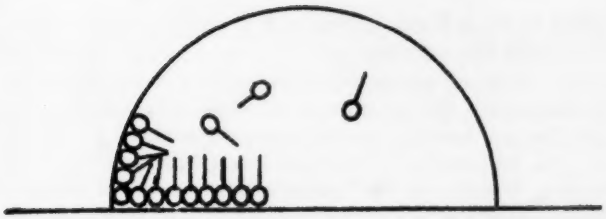

Figure 6. Molecular orientation at liquid-solid and liquid-gas interface

in the benzene and the carboxylic groups in the water. Actually, the orientation is several molecules deep; however, it is not necessary to go into deep depth orientation at this time.

Methods for Preparing Oriented Monolayers

Zisman, and co-workers, (16) reported the deposition of condensed oriented monolayers which were autophobic to the solution from which the layers were deposited. Chemically clean platinum paddles were dipped into a solution of stearic acid in highly purified n-hexadecane. Upon withdrawal from the solution, the substrate appeared to be unwetted by the solution; it exited dry. A drop of the solution formed a discrete contact angle of some 70° on the deposited monolayer. Zisman called the monolayers oleophobic films. The same results were obtained with highly polar molecules from n-hexadecane. When benzene was utilized, the samples did not exit dry from the solution.

Zisman, and co-workers (17), in a similar manner prepared hydrophobic films from aqueous solutions. Obviously, lower molecular weight materials were used.

In addition, Zisman (18), found that condensed monolayers could be prepared by dipping chemically clean solid substrates into molten organic material. A critical temperature, τ, was found at which the substrate exited dry and, apparently, clean from the melt. Observation of the contact angle or measurement of the film thickness (19) indicated a monolayer.

Many years before, Blodgett (20) had developed a technique for transferring monolayers from the surface of a liquid onto a solid substrate. The liquid surface of a Wilhelmy film balance was swept clean and the sample to be coated was deposited beneath the liquid surface. A drop of stearic acid-benzene solution was

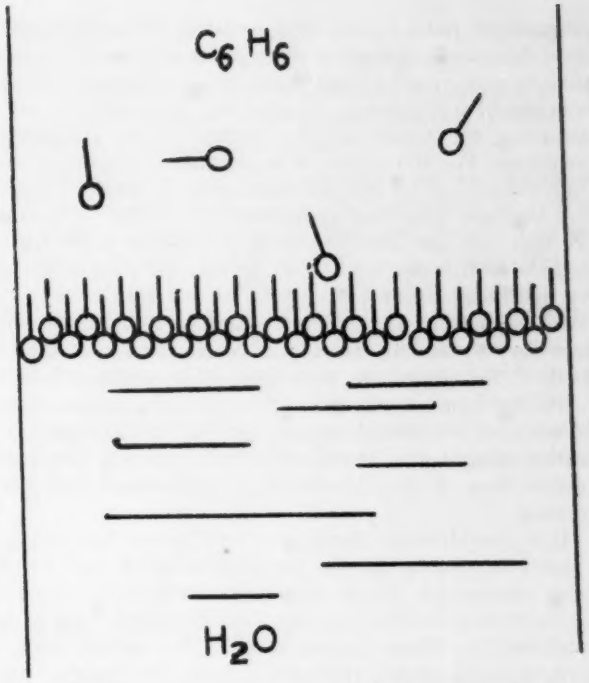

Figure 7. Orientation of stearic acid at a benzene-water interface

deposited onto the surface, and immediately spread to a two-dimensional gaseous film, *Figure 8a*. The sweep bar was moved toward the trough end of the tray compressing the stearic acid film and causing it to become oriented, *Figure 8b*. Once condensation of a two-dimensional solid film was reached, the submerged sample was removed through the film on the surface, depositing exactly a monolayer onto the solid surface. Should additional layers be desired, the dipping in and out is continued with a monolayer depositing on the dipping as well as the withdrawal step.

Sample Preparation

In any examination of adsorption it is important to have completely reproducible surfaces. Minor amounts of contamination make accurate interpretation of data extremely difficult. Whether powdered or planar surfaces are being utilized as the substrate, a method of

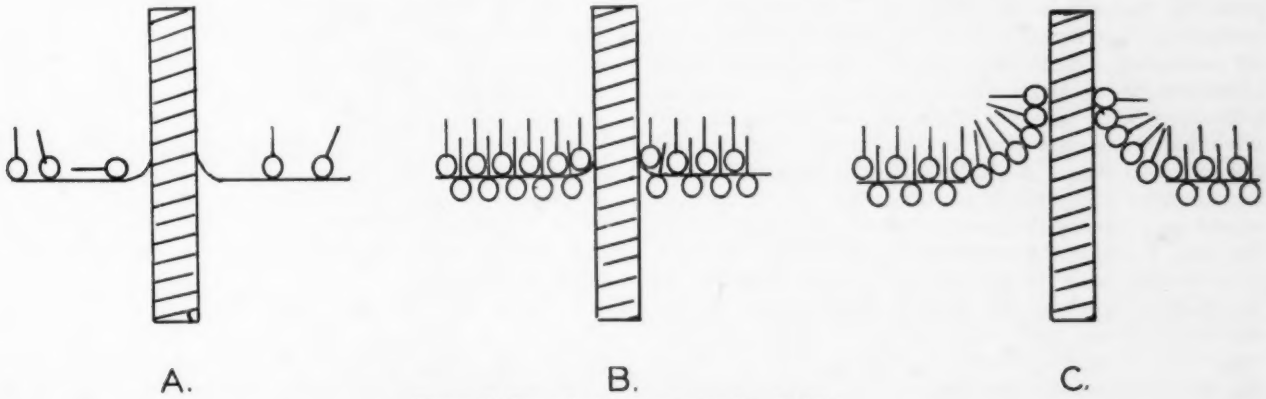

Figure 8. Transferring a monomolecular film

preparation must be selected and the subsequent work must be based on such a method. It is virtually impossible to remove all of the water from a surface and the majority of investigators consider the surface to be pure, assuming the water on the surface to be a standard condition. For the purist, it is possible, by roasting and high vacuum or by ion bombardment, to obtain a water-free surface. One frequently wonders if the techniques are that absolute and perhaps it is better to saturate the surface with water initially to be sure that reproducibility will be realized.

In preparing a powdered surface, it is frequently necessary to assume the degree of cleanliness. A typical method for preparing powdered glass utilizes E-glass marbles which are carefully cleaned and are then powdered in a controlled atmosphere (21). Generally, no further cleaning is necessary although one is not completely sure of the cleanliness of the system with this method.

It is considerably simpler to carry out a cleaning program with planar samples. Typical samples may be cut from microscope slides, degreased with triply distilled benzene in a Soxhlet extractor, and flame cleaned in an oxidizing gas flame. Examination of the sample with a contact angle device indicates a zero (0°) angle. Further, low angle (45°) examination with an ellipsometer yields reproducible results.

One might well inquire as to why adsorption studies are not carried out utilizing glass fibers. Experiments carried out by the author and others (21) indicated too much occluded material in the fiber interstices to yield reproducible results. In addition, one can do little else with a sample, as is the case with powdered samples.

Measurement Methods

There are several methods for determining the amount of material which has adsorbed onto the substrate during the adsorption phase. One may utilize a method described by Hackerman, et al (2-3), in which the weighed, powdered material is removed from the adsorbing solution, vacuum filtered and dried while dry air is passing over the powder until a constant weight is obtained. An adsorption isotherm is prepared by obtaining points for various solution concentrations plotted against the weight adsorbed per gram of adsorbent.

Still another method is to analyze the supernatant solution interferometrically (4). Another method concerns the use of infrared techniques; observing the concentration of material in solution, following adsorption, by measuring a particular peak (5). An example is the measurement of the carbonyl peak at 5.73 microns, calibrating with solutions of known concentration, and obtaining a typical plot of density versus concentration. Shepard and Ryan (6) utilized radiotracing techniques to determine the amount of adsorption which had occurred by counting the sample before and after adsorption and, knowing the concentration of labeled material. were readily able to determine the concentration of adsorbate. Greenhill (8) used a film balance as his measuring device and measured the surface area occupied by a known volume deposited as a condensed film on a surface balance before and after adsorption. By knowing precisely the volume of liquid which is applied to the surface, he was able to arrive at the concentration of the solution.

In preparing adsorption samples, it is a simple matter to determine the amount of adsorption on planar samples by any one of the above methods, except by weighing. In addition, one can take advantage of other techniques which are less suitable for powdered samples than for the planar type. In utilizing planar samples, Zisman, et al (9), have reported a number of papers in which the contact angle is used as a method for measuring the completeness of the adsorbed film. This method is most useful for monolayer adsorption or film balance transferred films. The objection, of course, to the contact angle has been that the zero angle is the ultimate. A second method involves radiolabeled adsorbates in which the planar samples are much more readily counted than are the powdered samples. In addition, by counting for very long periods of time, excellent statistics are realized. There are a large number of papers which have been reported concerning radiocounting; however, reference is made only to the Shepard and Ryan paper (6).

Still another method for observing the adsorbed material on planar samples concerns ellipsometry. This device is capable of measuring in the Angstrom range and has proven extremely useful on reflective substrates. By changing the angle of the instrument, it is possible to observe dielectric films less than 200 Angstroms thick on glass.

X-ray diffraction has been utilized for observing films deposited onto substrates; however, the ordinary technical individual will find it somewhat difficult to utilize this specialized technique requiring involved equipment.

When thicker films are investigated, a method which has been recently reported by W. T. M. Johnson (22) involves the careful abraiding of a surface with a metal pad using potassium bromide as the abrasive agent, collecting the potassium bromide and abraided material, compacting to a pellet, and observing in the infrared spectrometer. By carefully repeating, it is possible to plot a very significant curve of the change in adsorption as one abraids subsequently very thin layers from the surface of the film. This method should prove extremely interesting to the glass-reinforced resin manufacturers, especially where there is a possibility that certain components are bleeding to the surface of the film.

Harrick (23) has generated a method in which, in a specially designed cell prepared from silica or germanium, the film to be observed or a very thinly coated glass plate is layed on Sides A and B of the cell and infrared light is reflected into the cell. The infrared beam penetrates through the cell into the film a few Angstroms and the surface material may be carefully examined. In this particular case, one could imagine using monomolecular films of the resin deposited on to the glass in order that the surface or interfacial films could be analyzed.

Gottlieb has recently used the Zisman Vibrating Electrode to determine the surface coverage of planar samples by adsorbed materials (24). It is possible that a device of this nature could be modified so as to be useful with glass substrates.

In studying interfacial phenomena, the rate of desorption from a substrate is of considerable importance. As a typical example, Hackerman and Roebuck (3) determined the total adsorption and then by elution determined the irreversibly adsorbed material. Again, the gravimetric technique was utilized.

Ryan, et al (25), reported the rate of desorption of C-14 labeled fluorinated acids from solid planar surfaces. The desorption of the adsorbed film occurred at an appreciable rate from platinum, quartz, and glass as a function of the polarity of the solvent. Patrick and Payne (26) investigated a method for desorbing radiolabeled stearic acid from planar metal surfaces by a dynamic method utilizing a scintillation system. This method could readily be applied to glass substrates. As a matter of fact, the interference through reflection, which is somewhat of a problem with metal substrates, would be eliminated. The rate at which the radioactive count of the system increases represents the rate at which desorption from the solid sample occurs. The effect of polarity on the rate of desorption and the effects of different surface preparations may be studied by utilizing a system of this nature.

Naturally, one may take advantage of the techniques and devices which have been mentioned previously such as determining the change in contact angle as a function of the depletion of the adsorbed surface film. The ellipsometer may be used; radiocounting of the samples in air; and change in the surface potential. One point that should be made abundantly clear is the necessity of utilizing as many techniques as is possible in order to more completely define the system with which one is working, because of the very great difficulty of knowing precisely the roughness, cleanliness, and chemical structure of the system.

Part II

APPARATUS AND TECHNIQUES

A general description of the special equipment and techniques needed is included

The Automatic Film Balance —Wilhelmy Type

In all of the work associated with the investigation of thin films on surfaces, it is desirable to have a single method which is completely reproducible. The surface chemist is fortunate to have at hand an instrument which can be utilized to deposit films of relatively well-known structure up to several hundred layers in thickness. This instrument is known as the film balance. Because it is the only method by which known films may be deposited, it will be considered in some detail. In addition, it serves as a standard by which samples are prepared for calibrating the ellipsometer and for a contact angle control and surface potential determinations.

There are two general film balances which are used: the Langmuir and the Wilhelmy. The first utilizes a floating barrier and measures the difference in horizontal pressure exerted by a film coated area on one side and the uncoated area on the other side of the barrier. The second balance measures the surface pressure exerted on a paddle which dips vertically into the liquid substrate. The pressure in either case is plotted as a function of area to give pressure-area curves, *Figure 9*. When the Wilhelmy balance is utilized, it is possible to deposit oriented monomolecular layers of small molecules or polymers.

The film balance is shown schematically in *Figure 10*. The dipping instrument is shown in *Figure 11*.

Ellipsometry

The ellipsometer, or polarizing spectrophotometer, *Figure 12*, permits the measurement of extremely thin dielectric films which are deposited onto a reflective surface. As long as the films have average refractive indices and absorptivities differing from those of the substrate, film thicknesses may be measured. By setting the angle of incidence at 45°, one is able to utilize the instrument to observe dielectric films on planar glass.

In general, the ellipsometer consists of a series of elements which rotate about an optical axis, *Figure 13*. The plane of the substrate surface is at this optical center. An essentially monochromatic light source (L) illuminates the sample with plane polarized light produced by

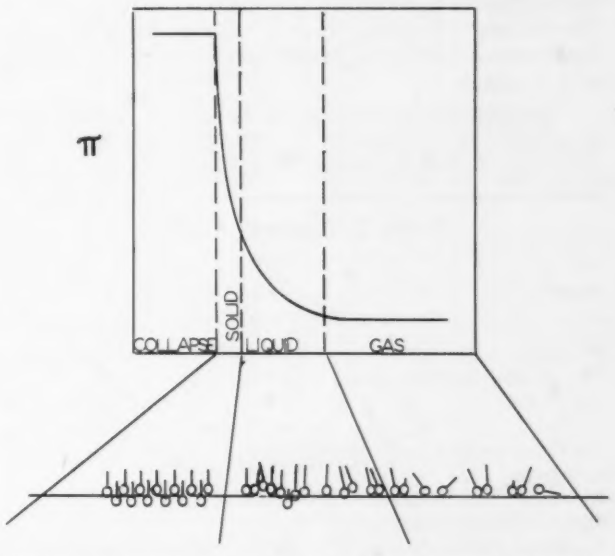

Figure 9. Pressure (π)—area curve for monomolecular film spread on water

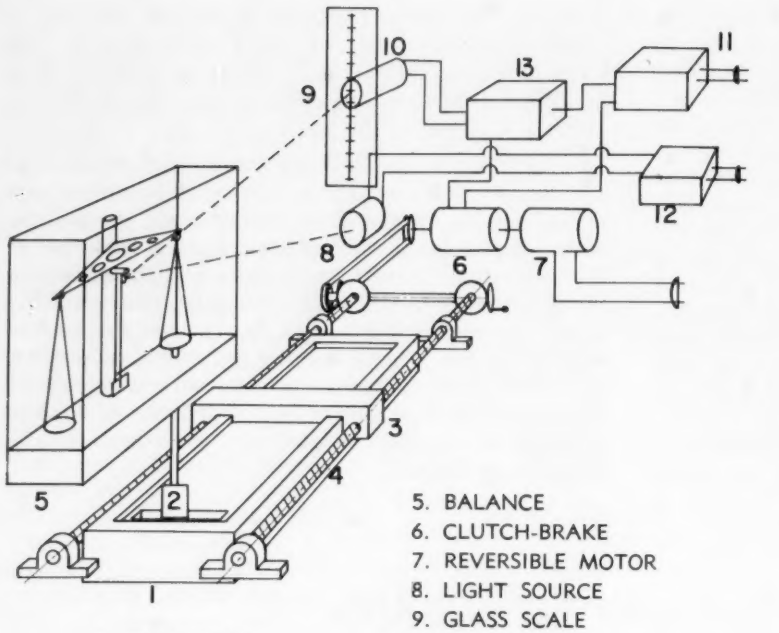

Figure 10. Schematic of a constant pressure film balance

the polarizer (P). The summation of the rotation of the two planes is directly proportional to the film thickness. The instrument is quite capable of differentiating film thicknesses of 0.2 A° (0.000000002 cm.).

Contact Angle Determinations

In order to accurately determine contact angles, it is necessary to have an instrument, *Figure 14*, which is capable of resolving the image of the droplet as near to the surface as is possible. The instrument developed by the Surface Chemistry Branch of the Naval Research Laboratories (16) is as simple and yet accurate a device as is available.

"The instrument consists of a horizontal optical bench on which the components are grouped into three independently mounted assemblies: (1) The optical system, comprising a horizontal low-power telescope with rack and pinion focusing, into which has been built a direct-reading goniometer head having two independently mounted crosshairs. (2) The specimen stage having provision for positive control of motions in both a vertical and a horizontal direction transverse to the optical axis. In addition, incorporation of a modified universal joint to permit tilting of the specimen stage facilitates examination of specimens which are not parallelepiped. (3) The illuminating system includes a readily adjusted light source, suitable heat and color filters, and an iris diaphragm.

"The heart of the optical system is the direct-reading goniometer head built into the telescope. Two crosshairs, each mounted as a diameter of the telescope, are so supported that each can be independently rotated in a plane perpendicular to the telescope axis. The plane of rotation of one crosshair is only slightly displaced from that of the other so that the eyepiece can be adjusted to bring both crosshairs into focus at the same time. As one crosshair is rotated, a 360°-scale rotates rigidly with it in a plane at right angles to the telescope axis, the scale being adjusted with its zero degree mark parallel to the crosshair. As the other crosshair rotates, a pointer rigidly attached and parallel to it, also rotates about the telescope. The angular displacement is then read directly from the scale.

"The telescope dimensions are chosen so that standard lens fittings can be used for both the ocular and the ob-

Table 2. Contact Angles

Material	θ_A	Remarks
Paraffin	91	No special preparation
Poly (methyl methacrylate)	67.5	
Tin Plate	78.4	Indicates considerable organic contamination
Tin Plate, washed in benzene	79.9	
Ferrotype	72.1	
Ferrotype, Talc Scrubbed	67.5	
Ferrotype, Al_2O_3 Scrubbed	21.4	
Ferrotype, Teflon Coating	80.1	Lightly rubbed with Teflon

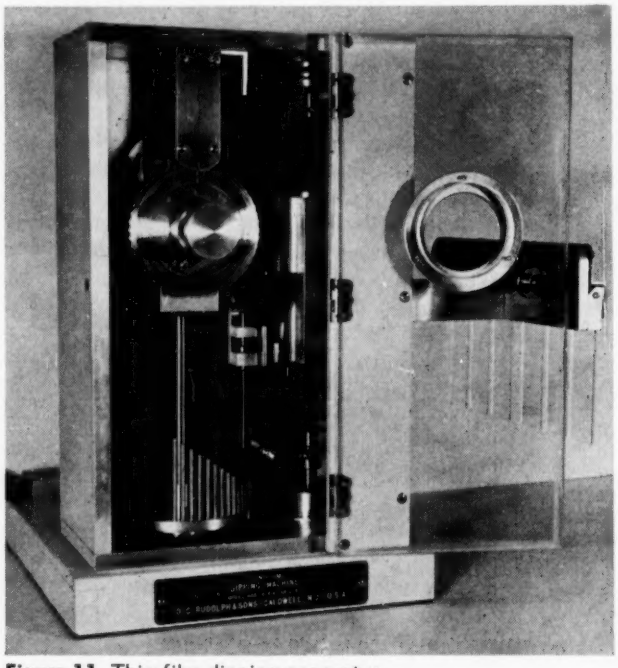

Figure 11. Thin film dipping apparatus

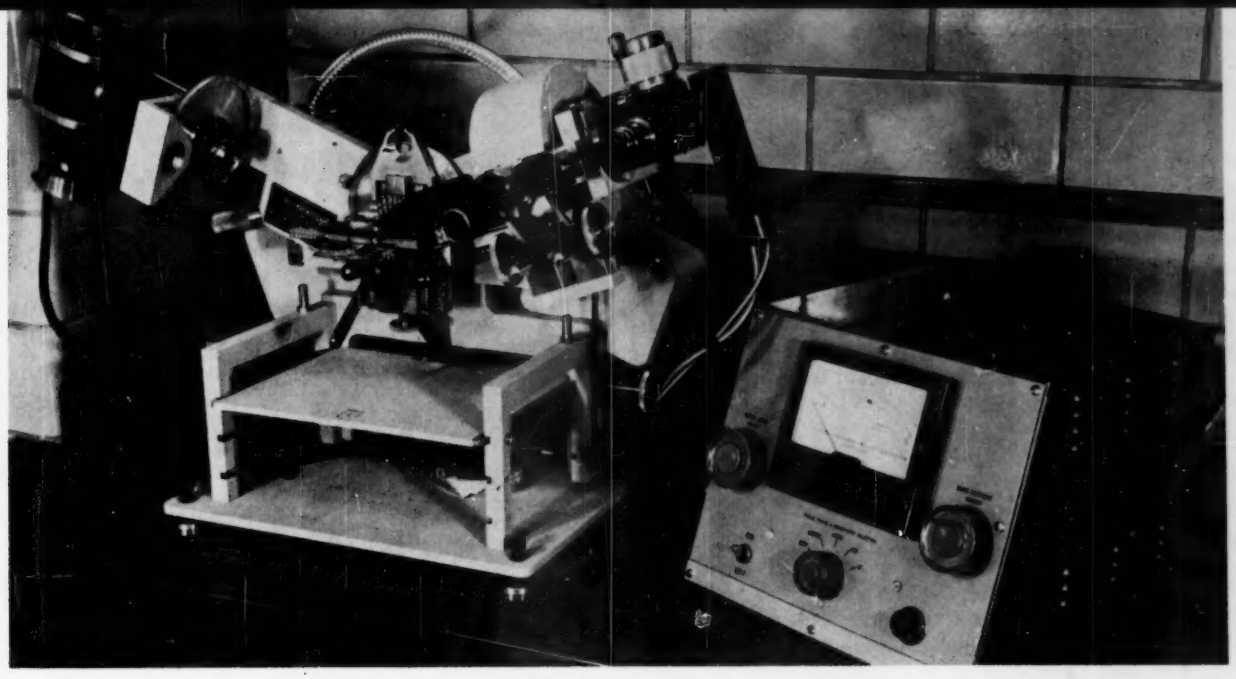

Figure 12. Ellipsometer

jective, with provision for the use of draw-tube adapters so that different combinations of focal length lenses can be employed. A fairly stiff fit is desirable for the tube carrying the eyepiece so that accidental jarring during measurements will not shift the focal plane. A positive locking device is desirable but permanent positioning of the eyepiece cannot be tolerated.

"Although the optical-bench mount permits large changes in the relative position of the telescope and the specimen stage, fine focusing is provided by a rack-and-pinion mechanism connecting the telescope to the top of the support column rising from the Cenco bench carriage.

"The specimen stage is a rectangularly shaped flat surface suitably mounted on a sturdy supporting column. A vertical motion of several inches is provided by a height-adjusting capstan arrangement involving a keyed cap and screw with key-way built into the hollow support column between the stage and the Cenco bench carriage. Transverse horizontal motion is provided by a second mechanism involving screw and key-way. A system of screw supports and modified universal joint provides a leveling device." (27)

Using water as the contact angle liquid, values of θ_A were obtained (*Table 2*). The angle represents the value reached when additional water added to the drop does not cause a change in the angle. Fifty (50 μ liter) drops were used as the starting size.

The effect of abrasive materials in cleaning surfaces is shown by the values reported for ferrotype. Light rubbing with Al_2O_3 (alumina) (γ-alumina) causes a reduction from 72.1 to 21.4° Continued rubbing would reduce the value to zero or complete, instantaneous wetting.

Radiotracer Techniques

The advent of the technique of C-14 labeling has proven to be a very useful tool. In the field of surface chemistry, it is fortunate that stearic acid is readily available at relatively low specific activity. Several methods are available for counting the radioactivity including radioautography, Geiger tubes, open window, and gas flow counting. In addition, the radioactive count of soluble systems may be determined by scintillation methods. The discussion of radiotracer techniques is sufficiently involved so as to be beyond the scope of this report. The reader is directed to "Experimented Nucleonics" by Bleuler and Goldsmith (28) or other suitable text books on the subject.

Desorption Methods

Desorption investigations may be carried out with either static or dynamic systems. Ryan, et al (25), reported excellent results utilizing static systems wherein the rate of desorption was determined by placing samples in the desorbing solution and removing them as a function of time. Patrick and Payne (26) have investigated a dynamic method wherein the sample is held in an especially designed cell so that the solution covers the sample without interfering with the counting method. A scintillating solution desorbs the film and the radioactive count of the solution increases in proportion to the removal of the material from the surface. The advantage of the system rests in the lack of movement which other systems require.

Application to the Reinforced Plastic Industry

Through judicious applications of several of the techniques, activation energies of adsorption and desorption

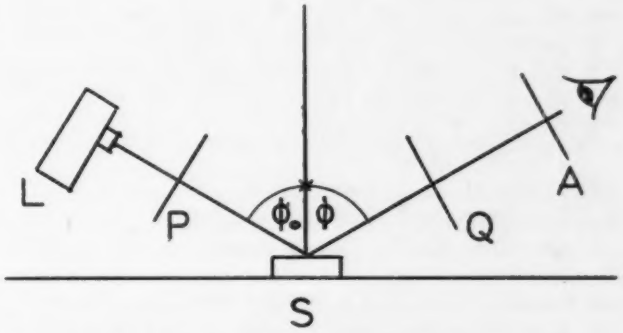

Figure 13. Schematic of ellipsometer components

of resin systems could prove useful. Rates of adsorption of various components of resin systems could prove important. By taking advantage of the instruments discussed and using model systems one could contribute markedly to the understanding of glass-resin interfacial interaction. More important, one could begin to understand the mechanisms of interfacial failure in glass-resin systems.

Several areas in which significant results could be achieved are suggested below:

1. The effect of glass surface treatments from a surface energetic viewpoint. Does the addition of a "tie coat" material result in a surface of markedly reduced surface energy? Does this reduction in surface energy come under boundary layers to be formed?
2. The utilization of radiotracers techniques with radiolabeled monomers and polymers to determine the adsorptivity of each component and to determine optimum monomer-polymer systems. Deuterated monomer and C-14 labeled polymer should be used to aid in simultaneous determinations of relative adsorptivity.
3. The utilization of infrared technique to examine adsorbed cured resin. Films of varying thickness can be built up and examined to determine difference between controlled "built-up" and conventional samples.

Conclusions

Applications of classical surface chemistry to the problem of glass-resin interfacial interaction is both plausible and practical. Techniques involving investigations of adsorption phenomena should produce very useful information.

Utilizing contact angle measurements, radiotracer techniques, infrared analysis, x-ray and electron diffraction and other specialized methods will contribute to the body of knowledge concerning interfacial phenomena and its practical ramifications.

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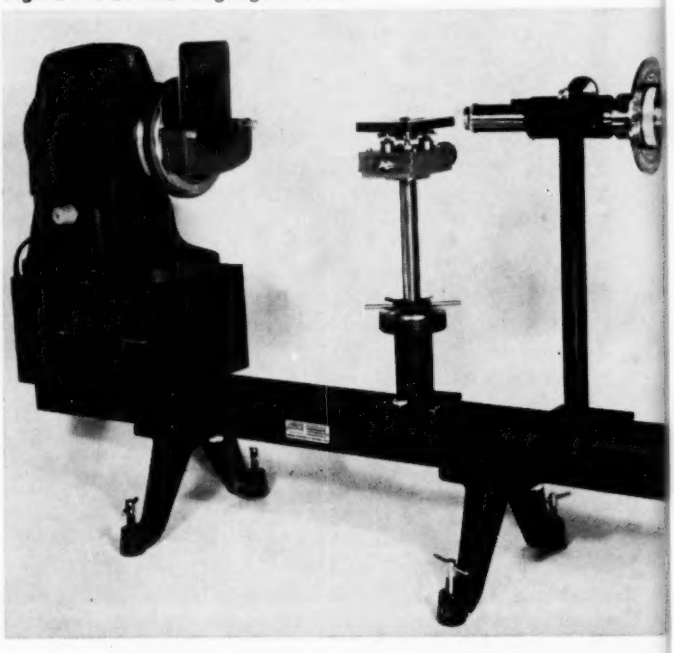
Figure 14. Contact angle goniometer



Study of the

Interaction of Organic Monomers and Water with Fiberglass

by Sorption Methods

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To understand fundamental aspects of reinforcement in glass-resin composites detailed knowledge of a great number of mechanical and chemical factors involved in the mechanism of reinforcement is necessary. Factors of considerable importance, are interface conditions and interactions between constituents in plastics laminates

The significance of chemical interaction between components in fiberglass-reinforced resins, with regard to the mechanical strength of the composite, may be better realized when requirements of good load transfer, usually expressed in terms of wetting and contact between constituents of the multiphase system, are considered from a physical chemical viewpoint. Here, the affinity of the reinforcing material toward the resin matrix, regarded in terms of interaction, may approach a limit in chemical bond formation. Although this condition must not necessarily be a prerequisite for good mechanical performance of a reinforced plastic, it undoubtedly represents a condition of optimum contact between components.

Mechanical Properties and Interfacial Conditions

The permanence of mechanical properties of glass-reinforced plastics, particularly their resistance to degradation on exposure to environmental influences, bears an even greater relationship to interfacial conditions. The reduction in flexural strength of a laminate, on prolonged exposure to high humidity is a case in point. Here, the observed deterioration of the composite, which has been reported less pronounced in glass laminates in which the reinforcing material received appropriate surface treatment (1, 2) seems to indicate degradation at the interface.

In view of the aforementioned relationships, a study of interface conditions in glass-reinforced plastics seemed desirable. Such an investigation was carried out by sorption measurements. Preliminary results (3) indicated a pronounced chemical affinity of E-glass toward organosilane finishes, while a study of bonding conditions between vinylsilane-treated glass and styrene, a representative resin monomer, disclosed relatively weak interaction. Since this was in apparent disagreement with the representation of alkenyl silanes as bifunctional coupling agents between the reinforcing components and resins, a more detailed investigation of reactions at glass-matrix interfaces became necessary.

The study presented here is concerned with the interaction of organic monomers with organosilane-treated fiberglass under consideration of bond conditions involved. Also, certain aspects of protection of glass-resin systems against the deleterious influence of water are investigated by sorption isotherm measurements on appropriately surface-treated substrates.

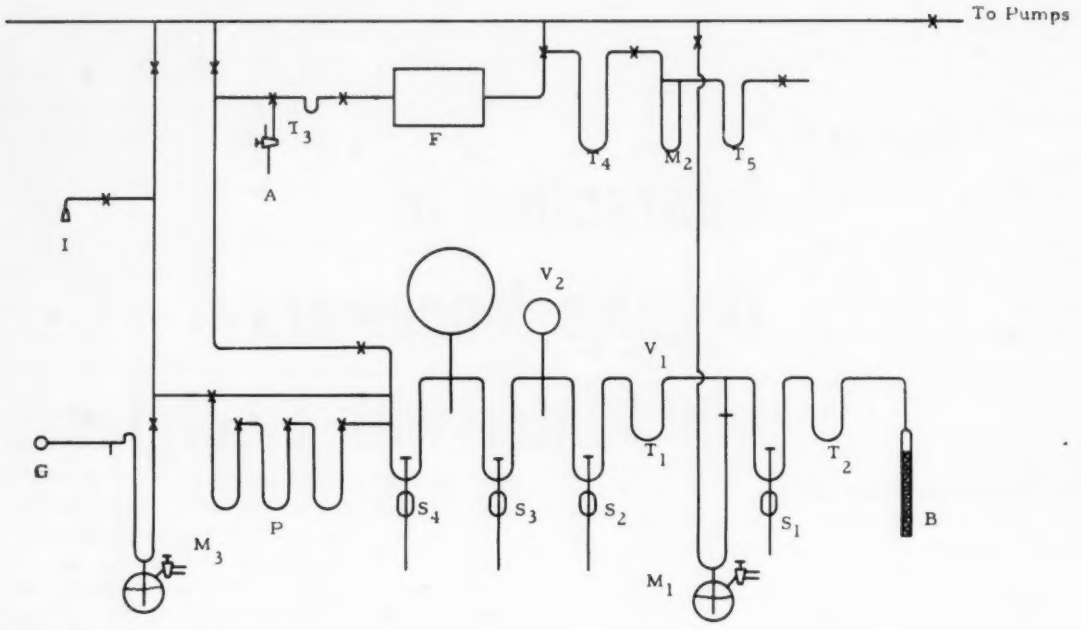

Figure 1. Schematic diagram of vacuum system

Materials and Methods

Reagents—Heat-cleaned E-glass roving was used consisting of 8 strands. Each strand containing 204 filaments of 0.00036 to 0.00040-in. nominal diameter comprised the substrate for sorption measurements. Samples with a surface area of 14 to 20 m^2 were prepared by winding the roving on a Pyrex spool according to a method described in a previous work (3).

Among the sorbates employed in surface reactions with E-glass and pretreated glass fibers were:

1. Vinyltrichlorosilane, $CH_2=CH_3SICl_3$
2. Vinyldimethylethoxysilane, $CH_2=CHSi(CH_3)_2OC_2H_5$
3. Styrene, $C_6H_5CH=CH_2$
4. Ethylene oxide, CH_2-CH_2 (O)
5. Epichlorhydrin, $CH_2-CH-CH_2Cl$ (O)
6. Di-tert-butyl peroxide, $(CH_3-C(CH_3)_2-O-)_2$
7. Water.

All organic compounds were purified by distillation and fractional condensation to eliminate interference of foreign materials with sorption measurements. Water, distilled from a potassium permanganate solution to destroy organic matter, was degassed by repeated freezing, pumping and melting.

Vacuum System—The apparatus shown in *Figure 1* is capable of handling relatively large quantities of reagents. It permits purification of sorbates and analysis of desorption products by combustion methods. The fiber sample is contained in a tightly fitting tube, B, which is connected to a manometer, M_1, by means of a mercury float valve, S_1. Additional valves are interposed at S_2, S_3 and S_4 to isolate reagents in calibrated containers V_1, V_2 and V_3 of 40-, 215-, and 1380-cc capacity, respectively.

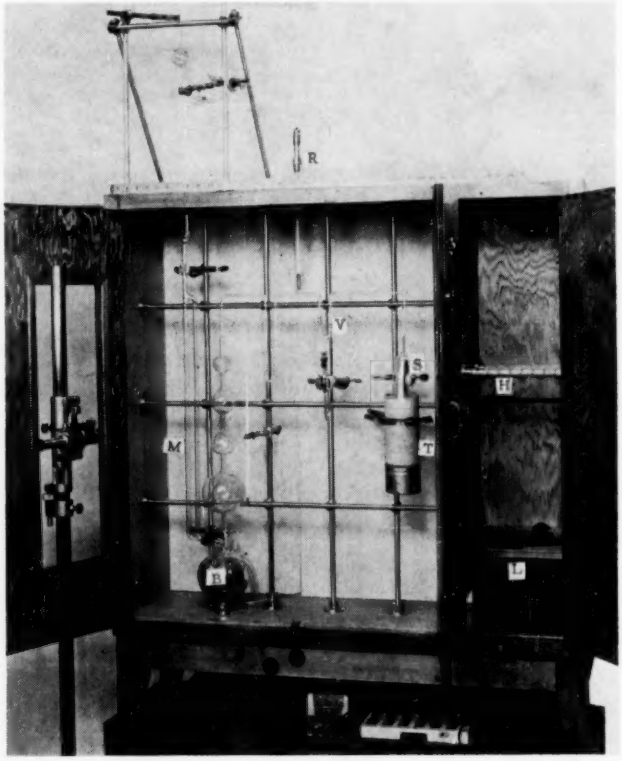

Figure 2. Temperature controlled BET apparatus

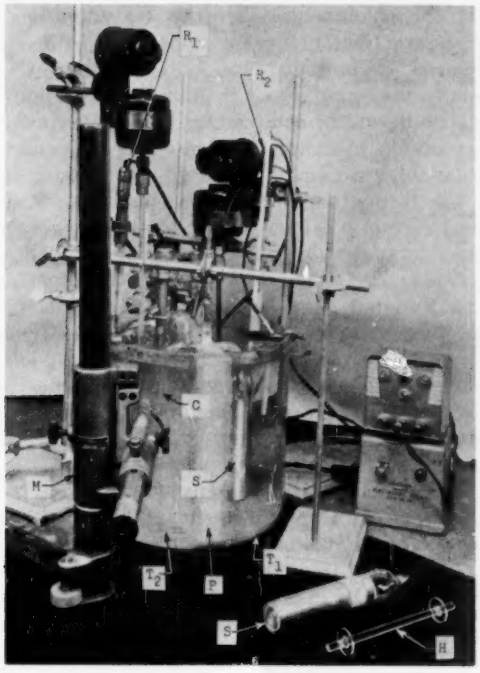

Figure 3. Apparatus for reaction rate studies

In operation, the reagent is admitted from a storage bulb at I. It is purified by fractional condensation in the train, P, and subsequently transferred to the sample. After exposure of the sample to the sorbate, the reaction products and excess of reagent are separated in the purification train. The composition of the mixture can be determined by volumetric measurements of combustion products obtained after oxidation of gases in the furnace, F, maintained at 900° C. The oxidation products are trapped in the tube, T_4, kept in a liquid nitrogen cryostat, while the excess oxygen is pumped through T_5 by a water aspirator. The pressure of the oxygen is monitored by the manometer M_2. After completion of the oxidation reaction, the amount of carbon dioxide is determined from the pressure that the gas exerts in containers V_1, V_2 and V_3.

Apparatus for Sorption Isotherm Studies—To shorten the time required for the establishment of equilibrium conditions in the adsorption of water vapor on fiberglass, and to permit determination of interaction energies from sorption isotherms obtained at different temperatures, a temperature-controlled BET apparatus was designed. The unit (*Figure 2*) represents a gas burette, B, consisting of five volume-calibrated bulbs, ranging in volumetric capacity from, approximately 25 to 850 ml. The burette, connected to a mercury manometer, M, is isolated from the sample, S, kept in a thermostat, T, through a mercury float valve, V. The glass specimen is attached to the apparatus after removing from it physically adsorbed water by heating in a boiling-liquid thermostat at 195°C and evacuating for 20 hrs. Connection of the evacuated sample-containing bulb to the apparatus is effected by destroying a break-off seal. The entire system is enclosed in a thermostatically controlled conditioning cabinet, in which a blower, L, provides air circulation throughout the interior, by conducting a stream of air through a 1000-watt nichrome heater, H, whose output is controlled by a powerstat and regulator, R.

Double Thermostat for Reaction Rate Studies—The reaction rate of styrene with organosilane-treated E-glass was determined with the apparatus shown in *Figure 3*. The sample, S, containing the glass roving tightly wound on the holder, H, is kept in a thermostat, T_1, at 30°C, while the tube connecting it with the sorbate, stored in a capillary, C, is maintained at 35°C in T_2. The styrofoam, P, partitioned compartments T_1 and T_2, thus provide a twin thermostat, with temperatures controlled by thermo-regulators R_1 and R_2 to ±0.05°C. The rate at which the organic compound in the capillary is expended by reacting with the glass sorbent is determined from the change in the height of the reagent column, as measured with a cathetometer, readable to ±0.005 cm.

Reaction of Styrene with Vinyltrichlorosilane- and Vinyldimethylethoxysilane-Treated Glass Substrates—The previously demonstrated (3) surface reactivity of vinyl- as well as methyltrichlorosilane-treated E-glass and the

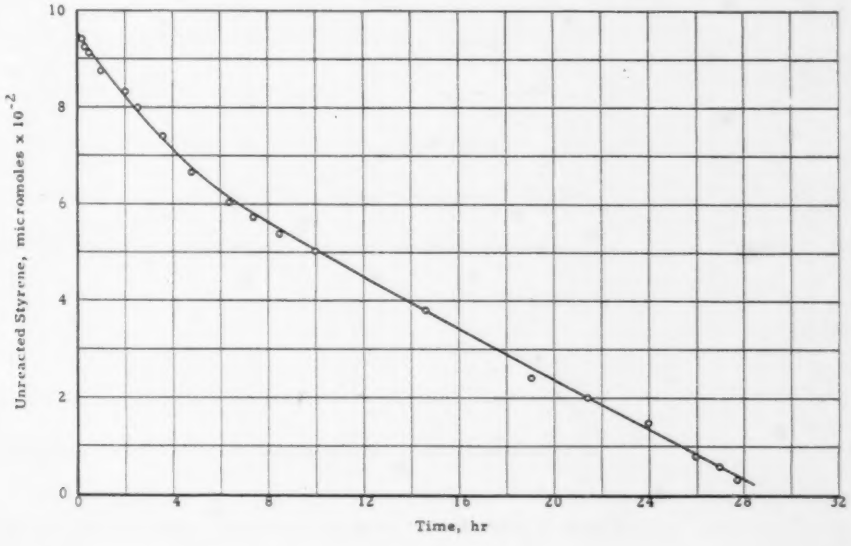

Figure 4. Reaction of 55% hydrolyzed vinyltrichlorsilane-treated "E" glass with styrene

Table 1. Polymerization of Styrene on Pretreated Glass Surfaces

PRETREATMENT OF E-GLASS SUBSTRATE			REACTION WITH STYRENE	
Surface Treatment	Exposure Duration hr	Surface Density micro-moles/m²	Reaction Rate micro-moles/hr	Specific Reaction Rate, m²/hr
Vinyltrichlorosilane	12	3.08	28	9.6
Vinyltrichlorosilane, 55% hydrolyzed	93	5.14	24	4.7
Methyltrichlorosilane	33	3.14	65	21.0
Methyltrichlorosilane, 90% hydrolyzed	20	3.22	10	3.1

extraction of polystyrene from the substrates by aliphatic solvents, suggested catalytic activity of compounds with a terminal Si-Cl linkage in the surface polymerization of monomer. To definitely ascertain the role which the vinyl grouping plays in the reaction of styrene with organosilane-treated fiberglass, several experiments were performed in which aromatic monomer was admitted to a partly hydrolyzed (chlorine-poor) vinyltrichlorosilane-reacted substrate, and to vinyldimethoxysilane-treated E-glass, representing a surface devoid of Si-Cl groups, but having a vinyl functionality.

The specific reaction rate (i.e., the rate per unit reaction site) of styrene with vinyltrichlorosilane-treated E-glass, as measured by the disappearance of monomer from the reaction system (*Figure 4*) was considerably less than the corresponding value obtained for the unhydrolyzed substrate (*Table 1*). The 50% reduction in the specific reaction rate, accompanying 55% hydrolysis suggests that further substitution of halogen by hydroxyl groups would change polymerization conditions of styrene from an ionic to a thermally initiated process. The drastic change in the reaction rate of unhydrolyzed and 90% hydrolyzed methyltrichlorosilane (*Table 1*) supports this argument.

A problem which required further consideration in the study of interactions of organic monomers with alkenylsilane-treated E-glass was the comparability of model experiments, as conducted in this investigation, with reaction conditions in commercial batch systems. As far as the exception to reactions of monomer with fiberglass in the gas-solid rather than liquid-solid phase is concerned, the distinction may not be justified, in view of the almost certain condensation of the gaseous reagent at the surface of the substrate. It is recognized, however, that polymerization of the resin in batch processes, which usually is initiated by a free radical mechanism, could produce different end-effects particularly in regard to the co-reaction of monomer with vinyl groups adsorbed at the substrate, than polymerization of styrene through an ionic scheme, as exemplified by the interaction of monomer on organohalosilane-treated E-glass, in the absence of a peroxide catalyst (1).

To simulate reaction conditions encountered in practice, consistent with requirements of model adsorption studies, a peroxide induced polymerization of styrene on poly(vinylsiloxane)-treated fiberglass was attempted. In the experiment, 110 micromoles of di-tert-butyl peroxide (more than 5% by weight of monomer) were pre-sorbed on a siloxane-treated glass sample and 2200 micromoles of styrene were admitted to the system. To increase the rate of polymerization, the temperature of the reaction tube was raised to 87°C, by placing it in the vapor of a trichloroethylene refluxing bath. In spite of this thermally favorable condition, the reaction did not proceed at a significant rate, and only after repeated condensation of unreacted monomer on the glass surface and prolonged exposure, did polymerization occur. The calculated average thickness of the polymer coating thus achieved, was equivalent to 28 monolayers, assuming a surface area of 32.9×10^{-16} cm² for the styrene molecule. Preliminary U.V. absorption measurements, after extraction of the polymer with a hydrocarbon solvent, indicated failure of styrene-to-vinyl bond formation. This corroborates the suggestion of preferential homopolymerization of styrene in systems containing vinyl and allylhalides, (4) and the data concerning the difficulty of copolymerizing styrene with coupling agents. (5, 6)

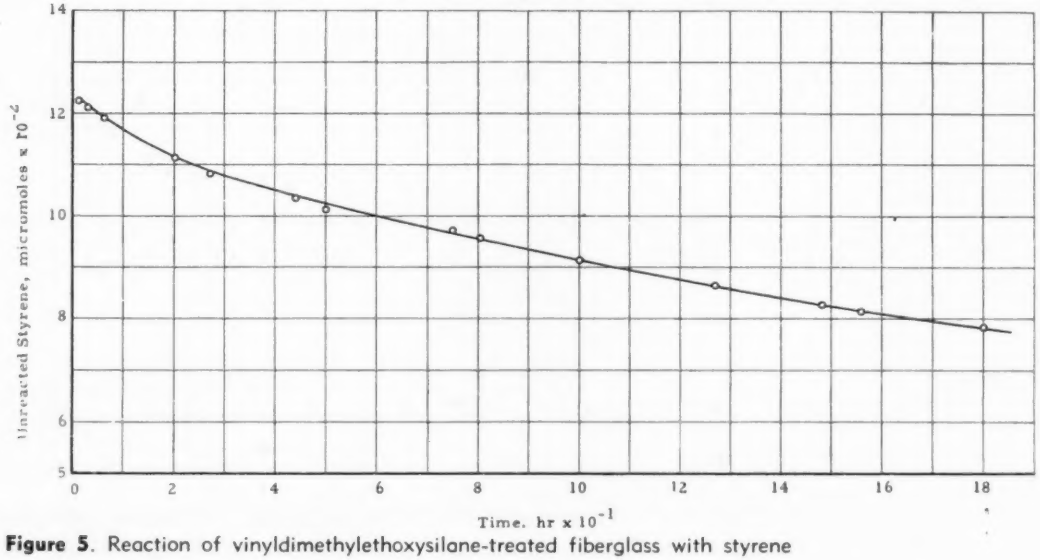

Figure 5. Reaction of vinyldimethylethoxysilane-treated fiberglass with styrene

The surface polymerization of styrene on vinyldimethlethoxysilane-treated fiberglass was performed under conditions paralleling those in previous reactions of monomer with vinyl- and methyltrichlorosilane sorbents, both in regard to surface concentration of organosilane and the amount of styrene admitted. The reaction rate (*Figure 5*) was extremely slow in comparison with the polymerization of styrene on organohalosilane-treated E-glass. Only 1.9 micromoles of monomer were expended per hour, after attainment of steady state conditions in the reaction system, corresponding to a specific reaction rate of 0.51 m^2/hr. This clearly suggests the passive role of vinyl groups in surface reactions involving styrene and places the responsibility for enhancement of monomer reaction with organosilane-treated fiberglass on the halide functionality of these compounds. To determine whether, in the absence of halogen, the vinyl group could have engaged in co-reaction with monomer through formation of a chemical bond at the glass-polymer interface, the vinyldimethoxysilane-treated, styrene-reacted substrate was subjected to extraction with n-heptane. Ultraviolet spectrophotometric analysis of the concentrated extract revealed presence of an aromatic compound with strong absorption bands at 252, 283 and 293 millimicrons, thereby providing evidence of no direct chemical interaction between vinyl groups and styrene, similar to conditions encountered in reactions with other organosilane compounds.

Sorption of Ethylene Oxide on Fiberglass

The pronounced reactivity of ethoxylene groups toward compounds containing active hydrogen atoms is responsible for the extensive use of epoxy derivatives in adhesive and interlaminar bonding applications. To obtain information on the affinity of epoxies toward proton-active groups on E-glass surfaces, a model experiment, using ethylene oxide as adsorbate, was performed.

After the usual conditioning at 150°C, a fiberglass sample of 15.1 m^2 surface area was exposed to 588.5 micromoles ethylene oxide for 19 hours at 28°C. On desorption at 29°C, 133.5 micromoles of the reagent were retained by the sample, yielding an apparent surface concentration of 8.8 micromoles/m^2. In order to explore bond conditions at the glass-ethoxy interface, a step-wise desorption was performed at progressively increasing temperatures, within a 100 to 350°C range.

Table 2. Desorption of Ethylene Oxide from Fiberglass

Time, hr	Temperature, °C	Cumulative Desorption, micromoles	
		Ethylene Oxide	Water
2.0	100	7.0	—
2.5	150	14.3	15.0
3.0	250	95.3	231.3
4.0	350	127.0	391.3

Table 2 indicates almost quantitative removal of the adsorbate upon heating to 350°C, with the bulk of the reagent recovered at 250°C. This, and the high initial surface density of the gaseous product on the substrate, suggests the possibility of surface polymerization of ethylene oxide without interfacial bond formation. The known thermal instability of polyoxyethylenes (7) and high molecular derivatives of formaldehyde supports the above argument.

Reaction of Epichlorhydrin with E-glass

To approximate more closely reaction conditions between commercial epoxy compounds and fiberglass, within the limitations of a model experiment, epichlorhydrin, a reaction component used in the manufacture of epoxy resins, was selected for sorption studies. Of a total of 447 micromoles of the reagent, admitted in a two-step sorption process, over a period of 195 hr, 280 micromoles were retained by the substrate after de-

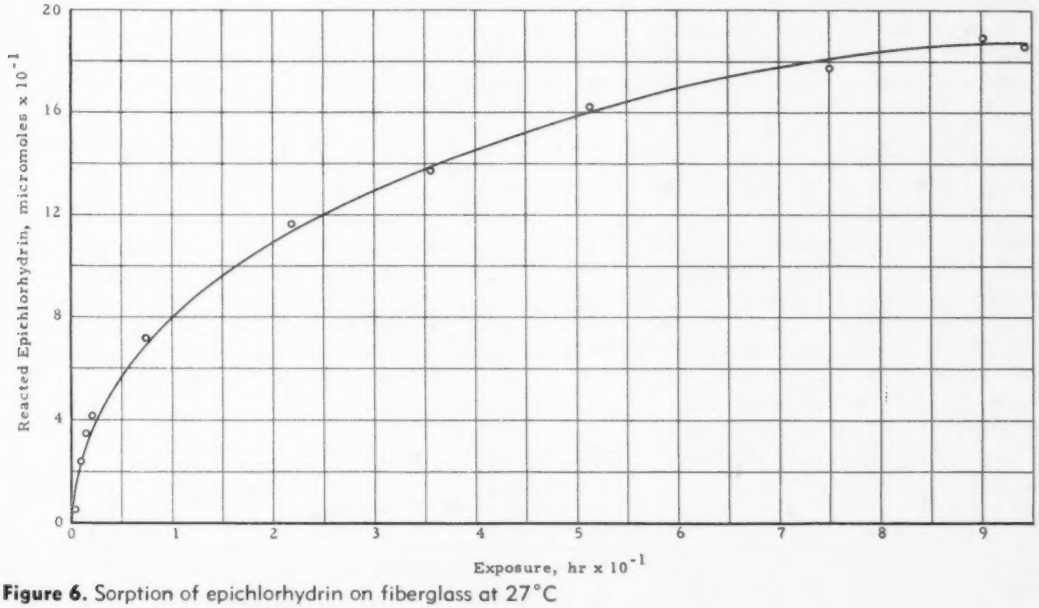

Figure 6. Sorption of epichlorhydrin on fiberglass at 27°C

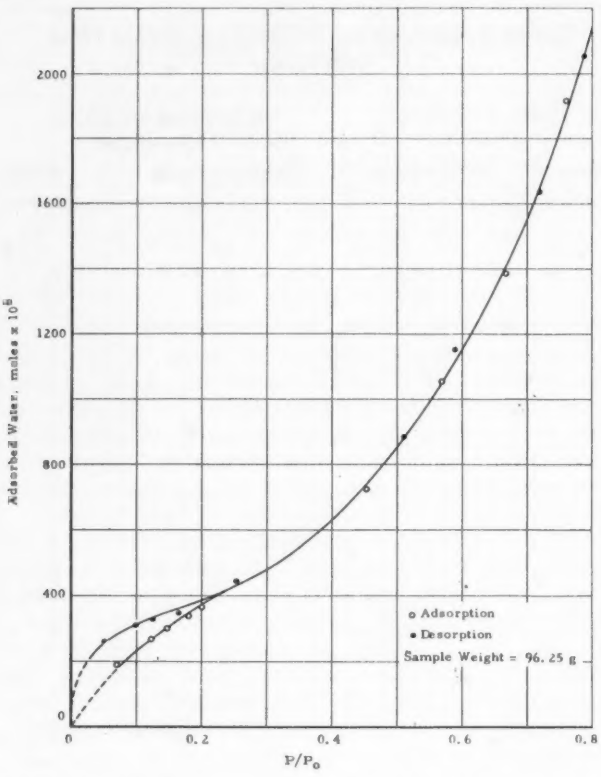

Figure 7. Adsorption of water on fiberglass roving at 50°C

sorption at 27°C. This represents an apparent surface density of 16.7 micromoles/m², equivalent to a nominal 2-monolayer coverage, assuming a spatial requirement of 25.8 Å² for an epichlorhydrin molecule, as calculated from:

$$A = (M/L\,d)^{2/3},$$

where A, M and d represent the surface area, molecular weight and density of the compound respectively, and L is Avogadro's number.

The process of epichlorhydrin reaction at the fiberglass surface is shown in *Figure 6*. Although the reaction rate after 1-hr exposure (13 micromoles/hr) appears considerably greater than at 80 hr (0.45 micromoles/hr), both rates, reduced to unit concentration of the sorbate present in the gas phase at the time of measurement, are essentially the same (0.06/hr), thereby suggesting first order kinetics.

It is interesting to note, by comparison with the previous experiment with ethylene oxide, that the glass-reacted epichlorhydrin aggregate could not be removed from the substrate by desorption at 150 and 250°C. Under more drastic conditions, at 350°C, 22 micromoles of epoxy monomer and 13 micromoles of hydrogen chloride were recovered. This behavior contrasts radically with the almost quantitative removal of ethylene oxide from E-glass on desorption at 250°C, thus suggesting considerable differences in the interfacial bond conditions of the two adsorbates. The presence of hydrogen chloride in desorption products implies involvement of the halogen group in the reaction and indicates the possibility of the existence of siloxane links between the organic compound and glass substrate.

Adsorption of Water on Fiberglass

The deterioration of mechanical properties of glass-reinforced plastics on exposure to moisture (8, 9) has been attributed to the weakening of glass fibers (10) and to the degradation of the interfacial bond (11) under the influence of humidity. Considerable efforts were directed toward improving mechanical performance of glass-reinforced plastics under conditions of use, and, as a result of intensive research in this area, several glass-treating compounds, intended for the protection of the reinforcing component from the detrimental influence of water and for the enhancement of interaction between constituents in glass-resin systems, were developed.

The hydrophobicity imparted to silica powder by treatment with organosilane compounds has been explained (12) in terms of interaction of surface silanols with alkylsilane reagents. It was pointed out, (3) how-

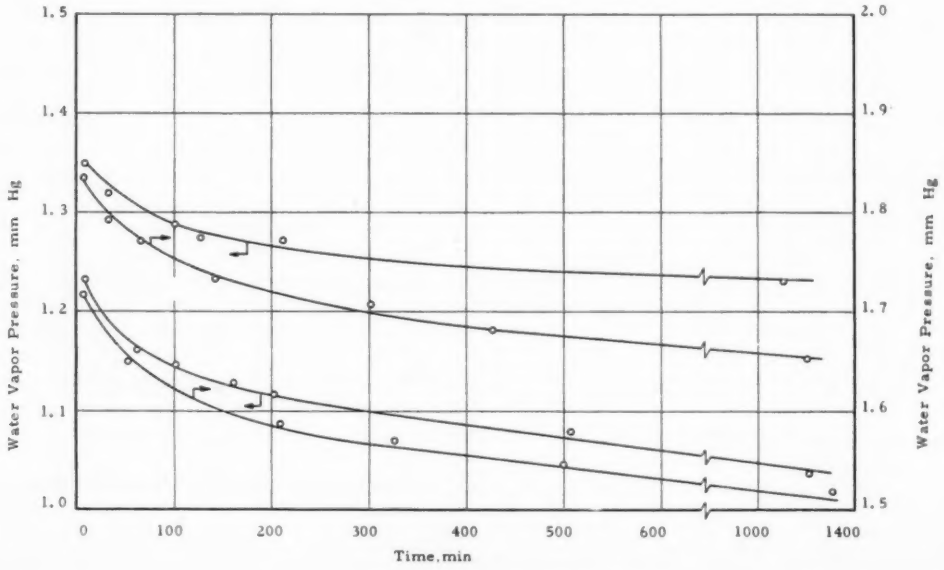

Figure 8. Progressive hydration of E glass at 50°C

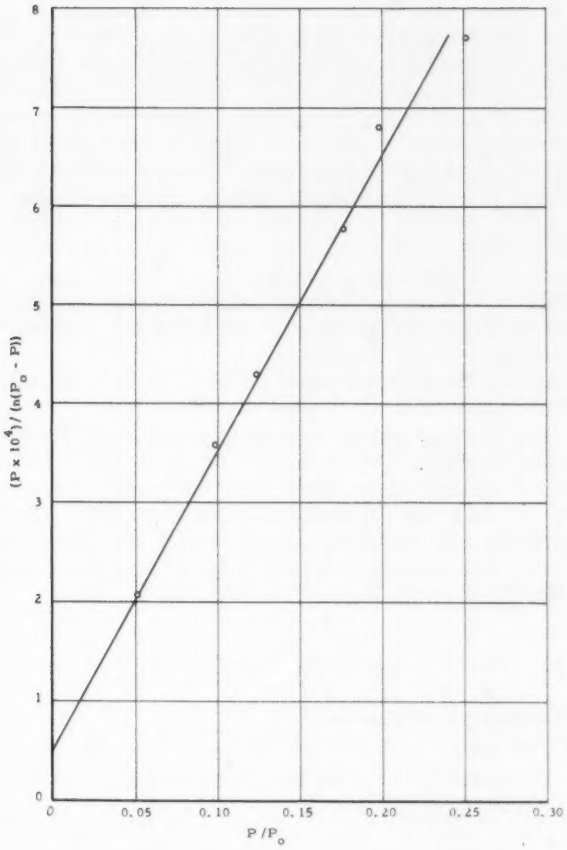

Figure 9. BET plot for adsorption of water on fiberglass at 50°C

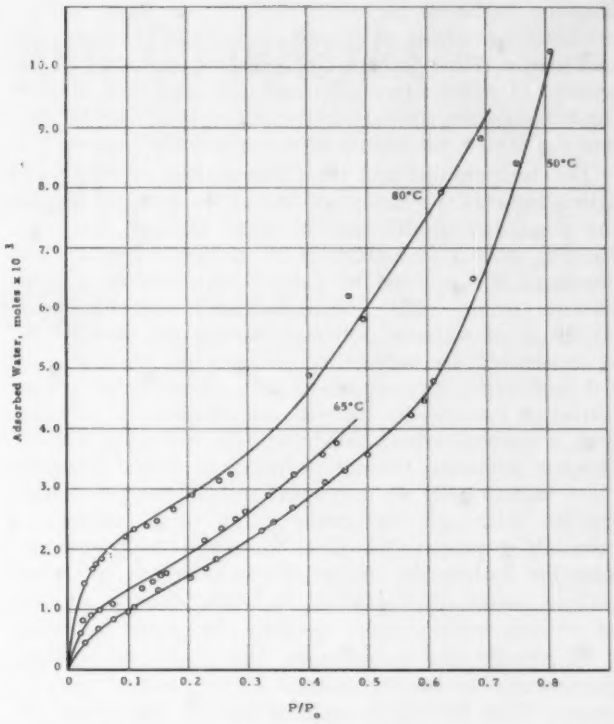

Figure 10. Adsorption isotherms for water on vinyltrichlorsilane-treated "E" glass at different temperatures

ever, that in E-glass, blocking of hydrophilic groups by organohalosilane treating agents may not be complete, because of the presence of moisture-sensitive cationic sites (Ca^{++}, Mg^{++}, Na^{+}) on fiberglass.

To determine the moisture affinity of the siliceous substrate in its original and surface modified form, sorption isotherm studies were conducted on heat cleaned and organosilane-treated, E-glass, with water vapor as adsorbate. The sorption isotherm for heat-cleaned roving is presented in *Figure 7*. The lack of coincidence between the adsorption and desorption branches of the isotherm at relative pressures (P/P_o) below 0.25 are attributed to the incomplete equilibration of the system and to the irreversible hydration of the sorbent in the initial stages of exposure. The reaction of the substrates with water is shown in *Figure 8;* adsorption is accompanied by a rapid drop in pressure within the first 30 min of exposure, followed by a slow decrease in pressure over a period of 20 hours. Assuming a cross section area of 10.5 $Å^2$ for a water molecule, surface coverage by 1, 3, 5 and 7 monolayers of adsorbate on fiberglass, at 50°C, is achieved at 10, 50, 65 and 77% relative humidity, respectively. This condensation of water vapor is greater than the reported (13) water adsorption on a borosilicate glass, on which coverage by three molecular layers was achieved at a P/P_o-value of 0.5, at 25°C. To obtain information about the heat of adsorption of water on E-glass under equilibrium conditions, a BET plot, utilizing the multilayer adsorption equation (14) was made (*Figure 9*).

$$P/n(P_o - P) = 1/n_m C + (C-1) \cdot P/P_o/n_m C$$

The quantities P and P_o represent the pressure of the system and the vapor pressure of the adsorbate at the temperature of the experiment respectively, n is the number of moles adsorbed, n_m is the number of moles of adsorbate required for monomolecular coverage and C is exponentially related to the heat of liquefaction, q_L, of the adsorbed vapor by,

$$C = e^{(q_1 - q_L)/RT}$$

where q_1 is the heat of adsorption for the first layer, R is the gas constant and T is the absolute temperature. The net heat of adsorption for water on untreated fiberglass, thus obtained was 2,665 cal/mole, and the number of moles forming a monolayer on the glass sample was 308 x 10^{-6} or 16.6 x 10^{-6} per square meter of substrate. The area occupied by a water molecule, calculated from monolayer coverage, was 10.02 $Å^2$, which is in fair agreement with the accepted value of 10.5 Å (2) (15).

The hydration behavior of vinyltrichlorosilane-treated fiberglass was also investigated by sorption methods. Treatment of the glass specimen involved its exposure for 16 hr to a moisture-saturated air stream under aspiration at 20 mm Hg and 23°C, at a rate of 1 cm^3/sec, and subsequent admission of vinyltrichlorosilane for 15 hours, at a comparable rate, so as to effect deposition of a substantial polysiloxane coating on the E-glass sample.

Sorption isotherms for water obtained on these, surface modified specimens at 50, 65 and 80°C, (*Figure 10*) indicated a rather unexpected behavior, inasmuch as the amount of water vapor adsorbed increased with increasing temperature, contrary to the principle of Le Chatelier and the exothermic nature of the adsorption process.

The temperature and time dependence of this interaction between substrate and absorbate strongly suggest the possibility of diffusion of water through the polysiloxane coating (estimated at 10 molecular layers). The argument is supported by gas diffusion studies of polysiloxane resins, (16) which indicated relatively small resistance of siloxane polymers toward gas permeation, as evidenced by activation energies of the order of 1-3 kcal/mole, in comparison with considerably higher activation energies for the diffusion of gases in polymers with a carbon-carbon backbone. The diffusive transfer of water molecules through polysiloxane coated fiberglass plays undoubtedly an important role in the permeation process. Although the configuration of a polymer is primarily responsible for diffusion, in glass supported systems the hydrophilic nature of the substrate and presence of chemically unreacted, moisture sensitive sites on its surface, could further enhance the water transport.

Admittedly, the polysiloxane film thickness on fiberglass treated by the commercial dipping method may be greater than the thickness obtained by the vapor exposure technique used in this study. These differences, however, should influence time relationships in the hydration and possible degradation of the system without affecting the mechanism of permeation. The delay in the ultimate interaction of glass with water, brought about by an interfacial barrier of finite thickness, invites the often posed question about the extent of protection against moisture afforded to fiberglass not only by the treating compound, but also by the resin matrix. This problem is currently being investigated in comparative sorption studies of water vapor on polysiloxane coated and vinyltrichlorosilane-treated, styrene reacted E-glass.

Summary

Adsorption studies on vinyltrichlorosilane-treated E-glass roving, with styrene as adsorbate, indicated a pronounced dependence of the reaction rate on the initial extent of hydrolysis of the halosilane-reacted substrate. Substitution of halogen with hydroxyl groups in the surface-bound treating compound reduced the polymerization rate of monomer on the modified sorbent appreciably. A similar behavior was noted in samples pretreated with vinyldimethylethoxysilane, an organosilane compound devoid of halide functionality. This suggested a relatively passive role of vinyl groups in surface reactions involving styrene, and indicated preference of the reaction system toward polymerization by an ionic mechanism. Introduction of a peroxide catalyst to vinylsilane-treated E-glass, by preadsorption of di-tert-butyl peroxide on the polysiloxane coated substrate, did not greatly increase the reaction rate of styrene. The residual polymer, obtained above 80°C, could be extracted with a paraffin solvent, indicating absence of covalent bonding between vinyl and styrene, similarly as in reaction systems in which polymerization occurred without catalysts promoting reactions by free radical initiation.

Although polymerization of ethylene oxide was observed in its sorption on fiberglass, the bulk of the initially admitted reagent could be removed from the substrate by desorption at 250°C. This indicated thermal degradation of the polyether and suggested surface polymerization without interfacial bond formation. In distinction to this behavior, epichlorhydrin, which also exhibited a strong tendency toward polymerization on E-glass, could not be desorbed by heating in vacuum at 150 and 250°C. The thermal stability of the product and presence of hydrogen chloride in the desorbate suggested existence of relatively strong interfacial forces, possibly through direct involvement of the halogen group of epichlorhydrin in the reaction.

Adsorption of water vapor on heat cleaned and vinyltrichlorosilane-treated E-glass suggested progressive hydration of the siliceous substrate on prolonged exposure to the adsorbate. Surface-treated fiberglass exhibited enhanced adsorption at elevated temperatures. The temperature and time dependence of this interaction between substrate and adsorbate indicated that the permeation process was determined by diffusive transfer of water molecules through the polysiloxane film.

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The Chemistry of Chromium Complexes used as Coupling Agents in Fiberglass Resin Laminates

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Chemistry and structure of fiberglass surfaces . . .
Chemistry of the coupling agents themselves . . .
Interaction of the coupling agents with the surface . . .
Bonding of the treated surface to the laminating resins . . .
Effect of varying all factors on the strength and water resistance of the laminates.

Evidence available in the literature, coupled with work to be reported in this article, indicate that both the chemical and structural composition of the glass surface may differ markedly from that of the bulk phase.

Nature of the Glass Surface

Studies were made on a series of six glasses, all of which are commercially available in a fibrous or finely-divided, flake form. Each of them has been used in the past, at least to a limited extent, in preparing fiberglass laminates. One of the glasses is a high surface area, porous, almost pure silica glass,* another a type which is sometimes designated "Alkali Glass",** three are of the general "E" glass composition*** but differ in surface area, and the last is a very complex beryllium-containing type† which has an unusually high modulus.

These glasses were characterized by an analysis of their chemical composition, their surface areas by nitrogen or krypton gas adsorption (1), their degree of surface hydration by determining the water evolved on heating from 110° to 610°C., and by acid and base titrations to determine the number and strength of acidic and basic functional groups present on their surface.

The chemical composition, surface area, and water evolved are given in *Table 1.*

Figures 1 and 2 show the results of acid and base titrations of these glasses with 0.001 normal solutions of HCl and NaOH in 4 normal NaCl (2). Titrations were performed in polyethylene beakers with "Teflon" stirring bars to avoid the complication of glass equipment. The pH of the solutions was determined with a Beckman Model G pH meter using a calomel and a special glass electrode which has a negligible sodium ion error even at high pH in concentrated sodium salt mixtures.

The sample size of glass taken varied somewhat with the surface area of the glass, and ranged from 1.5 to 9.0 grams. All glasses were dispersed in 150 cc. of 4.0 normal NaCl. Prior to titration, they were chopped to relatively fine lengths by five minutes mixing with distilled water in a Waring Blendor and dried at 110°C. in an oven.

Figure 1 shows a blank titration and that of the six glasses as determined. In *Figure 2*, the data have been replotted for clarity in presentation, with all titrations starting from a common origin at a pH of 2.5. This plot shows the titration curves which would have been obtained had each solution been adjusted initially to a pH

* Heat cleaned and acid leached "E" glass fabric reduced to almost pure silica glass: Trade-mark Refrasil, by H. I. Thompson Fiber Glass Co., Los Angeles, California. Starch-oil size was a large portion of the Loss on Ignition (L.O.I.).

** An unsized tight fiber mat from Famco, Inc., Louisville, Kentucky.

*** "E" glass fabric: Style 181 with 112 or heat cleaned only as finish.

"E" glass flakes: 2.5 micron thickness, from Owens Corning Fiberglas.

"b" glass microfibers: LOF staple 106 microfiber, now Johns Manville.

† Imperial No. 905, Imperial Glass Company, Bellaire, Ohio.

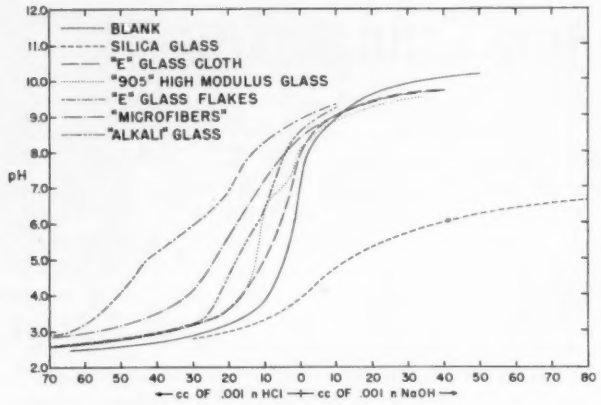


Figure 1. Acid-base titrations of various glasses in four normal sodium chloride solutions

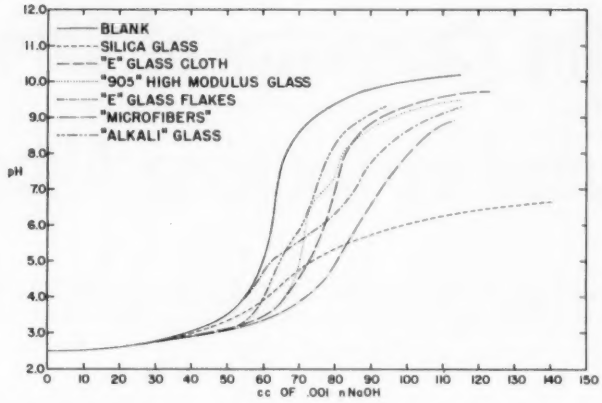


Figure 2. Titration of various glasses from a pH of 2.5 with thousandth normal base in four normal sodium chloride solutions

of 2.5 with HCl and then titrated with 0.001 normal NaOH.

Figure 3 shows a similar titration of one of the glasses (heat cleaned "E" glass cloth) in the absence of the 4.0 normal NaCl supporting electrolyte.

The purpose of using 4.0 normal sodium chloride as a supporting electrolyte in these titrations was to sharpen the breaks which would be obtained from the titration of polymeric surface acidic groups.

Previous work by one of the authors (3) had shown that silanol groups on amorphous silica surfaces behave as polymeric weak acids.

The reasons for this can be visualized by consideration of what happens during the titration of such a surface, as indicated in *Figure 4-a*. When one of the surface silanol groups is neutralized and becomes charged, the neutralization of the next group becomes more difficult. This is because a positively charged proton must be removed from the surface, not only against the chemical attraction of the SiO-group to which it is attached, but also against the electrostatic attraction it would have for the negatively charged surface. Obviously, the higher the charge on this surface, the larger is this electrostatic attraction. It thus becomes increasingly difficult to remove protons as the degree of charge already on the surface increases.

Mathematically, this is reflected in an apparently continually decreasing value for the acid dissociation constant. The effect of this on the pH titration curve is that a very poorly defined break is obtained if titrations are performed in the absence of neutral salts. As shown in *Figure 4-b*, if a large excess of neutral salts is present, the positively charged cations of the neutral salt will tend to screen the negative charges already present on the surface from their effect on the removal of further protons, and sharper titration curves are obtained.

Table 1.[1,2] Bulk Phase Chemical Composition of Various Glasses

	"Silica" Glass	"E" Glass Cloth[3]	"E" Glass Flakes	"E" Glass "Microfibers"	"905" High Modulus Glass[4]
% SiO_2	95.74	69.56	62.96	61.70	48.0
% Al_2O_3	0.88	11.82	16.78	7.49	—
% CaO	0.004	15.24	1.52	0.03	11.85
% TiO_2	—	—	8.65	6.85	4.0
% B_2O_3	0.59	6.74	7.42	8.29	—
% Na_2O	0.01	0.40	0.40	7.93	—
% MgO	—	—	—	—	8.15
% Li_2O	—	—	—	—	6.0
% BeO	—	—	—	—	8.0
% V_2O_5	—	—	—	—	4.0
% MoO_2	—	—	—	—	2.0
% L.O.I.	7.26	0.16	0.34	1.70	—
% Water lost on heating between 110°C. and 610°C.	4.0	0.12	0.11	0.73	—
Specific surface area in m^2/g.	47	0.12	0.18	0.79	—

NOTES:
(1) Constituents indicated by a dash were not present in appreciable amounts as shown by emission spectrographic analysis.
(2) All glass compositions recalculated on an anhydrous solid basis. That is, the loss on ignition (L.O.I.) was determined and the analytical data corrected to the values which would have been obtained after ignition.
(3) Our results gave a considerably higher silica analysis than has been reported for a typical "E" glass composition.
(4) Composition reported for this glass by private communication from W. J. Eakins, DeBell & Richardson, Inc.

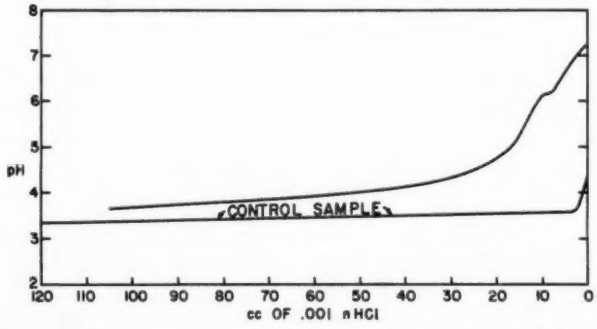


Figure 3. Titration of heat cleaned "E" glass cloth with 0.001n HCl in distilled H_2O

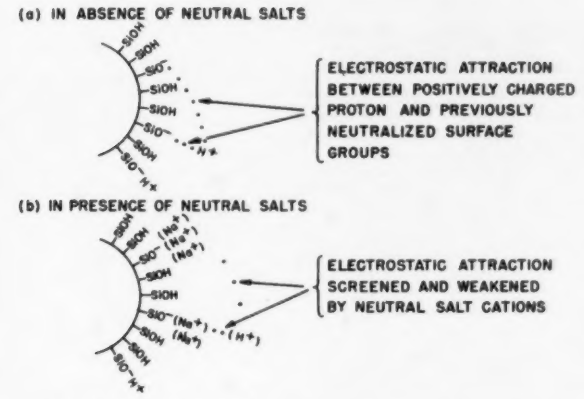

(a) IN ABSENCE OF NEUTRAL SALTS
ELECTROSTATIC ATTRACTION BETWEEN POSITIVELY CHARGED PROTON AND PREVIOUSLY NEUTRALIZED SURFACE GROUPS
(b) IN PRESENCE OF NEUTRAL SALTS
ELECTROSTATIC ATTRACTION SCREENED AND WEAKENED BY NEUTRAL SALT CATIONS

Figure 4. Neutralization of acid groups on an amorphous silica surface

A general equation can be derived which reflects the effect of neutral salts and the polymeric character of the surface silanol groups, and makes it possible to determine the number of silanol groups which are present on a surface and the fraction of the total which are ionized (negatively charged) for any conditions of added neutral salt content, neutralizing base, and pH. The equation which has been found to correlate these variables on amorphous silica surfaces is:

$$pH = 12.08 - 0.74 \log [Na^+] - 3.47 \log \frac{1-\alpha}{\alpha} \quad (1)$$

In this equation, pH is the negative logarithm of the hydrogen ion activity, $[Na^+]$ the activity of sodium or other monovalent cations in the system, and α the fraction of surface silanol (i.e., Si-OH) groups ionized. The value of α can be computed from a knowledge of the specific surface area "SA" of the sample expressed in square meters per gram, the number of surface silanol groups "n" per square millimicrons of surface, and the moles of surface reacted base per gram which is equal to the cc. of base/10^3 x normality of base, using "N" as a symbol for the normality of base:

The formula for computing α is:

$$\alpha = \frac{\dfrac{\text{cc of surface reacted base/gram}}{10^3}}{\text{SA x n x } 10^{15}} \text{ x N x 6 x } 10^{23} \quad (2)$$

for a 0.001 normal base; $\dfrac{1-\alpha}{\alpha}$ becomes,

$$\frac{1-\alpha}{\alpha} = \frac{\text{SA x n}}{\text{0.6 x cc. of base}} - 1 \quad (3)$$

It will be useful in discussing the results to solve equation (1) for the number of silanol groups per $m\mu^2$ of surface ("n"). Equation (4) is such a solution, and can be used to determine the number of silanol groups on an unknown surface if equation (1) is assumed to hold:

$$n = \frac{\text{0.6 x cc. of base}}{\text{SA}} \left[\left(\text{antilog} \frac{12.08 - 0.74 \log [Na^+] - pH}{3.47} \right) + 1 \right] \quad (4)$$

Once "n" has been determined, equation (1) can be used as a chemical method for determining surface area.

Before taking up the experimental titration curves which were found for the glasses listed in *Table I*, it might be best to examine their interpretation.

Titration Curve Interpretation

The general shape of the blank titration curve can be seen in *Figures 1 and 2*. This is a typical strong acid, strong base neutralization curve when the titration is performed with very dilute solutions of acids and bases. A single sharp break extends from a pH of about 3.5 to 8.5, with an asymptotic approach to the pH value of the acid and base titrating solutions, respectively, as limiting values.

If the solution being titrated contains no free acids or bases or only neutral salts of strong acids with strong bases, the titration curve should superimpose on the blank.

If free strong acids or strong bases are present, the curve would be displaced to the right or left, respectively, but would still have the same shape. The extent of the displacement to the right or left would be a measure of the concentration of the strong acid or base present on the surface.

If a salt of a strong base with a weak acid is present, the titration curve will be displaced to the left of the blank curve, and will have a different shape. An additional break will occur, the mid-point of which is located at a pH value approximately equal to the negative logarithm of the acid dissociation constant (pKa) of the weak acid.

If a free weak acid is present, the whole titration curve will lie to the right of the control curve, but again will have a break similar to that just described.

Examination of the titration curves in *Figure 1* of the six glasses, five of which are listed in *Table 1*, shows that the pure silica glass behaves like a weak acid, since the titration curve is displaced to the right of the control curve. The good agreement of the predicted theoretical curve using equation (1) (*Figure* 5), with the experimental titration curve, indicates that this pure silica glass has only silanol groups on its surface.

The remaining five glasses act like salts of strong bases with weak acids and have a more complex surface composition, since all show at least two breaks. They show one or more relatively well-defined breaks in a pH region from about 3 to 6, as well as a less pronounced break in

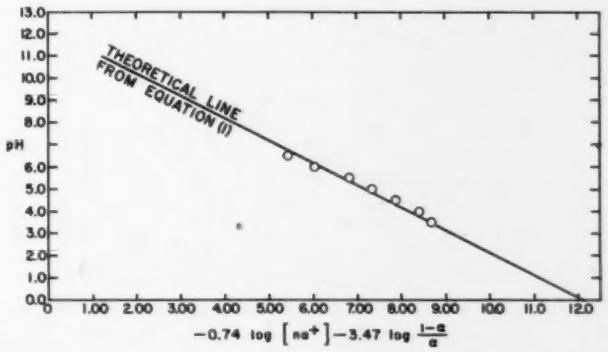


Figure 5. Test of equation (1) for predicting the titration curve of silica glass

Table 2. Surface Chemical Composition of Various Glasses

Material	Surface Area by nitrogen or Krypton absorption in $m^2/g.$	Water Molecules per sq. $m\mu$ using Surface areas by gas absorption	Silanol groups per sq. $m\mu$ using Equation 4	Surface Area by Silanol Titration using Eqn. 1* in $m^2/g.$	Surface Acid groups other than silanol groups per sq. $m\mu$**
Silica glass	47	283	16	100	0
"E" Glass cloth	0.12	333	7	0.16	5.7
"E" Glass flakes	0.18	216	64	3.54	3.2
"Microfibers"	0.79	329	13	2.96	3.6
"Alkali" glass	—	—	—	0.96	3.9
"905" high modules glass	—	—	—	3.29	1.4

* Assuming 8 silanol groups per square millimicron for "n"
** Using silanol titration surface areas from column 5.

the region of 7 to 9. The latter is probably from silanol groups as in the case of the pure silica glass.

It should be noted that since the sample sizes and surface areas of glass used in these titrations were different, the degree of displacement of the curve from the blank is influenced not only by the nature of the surface groups present, but also by the surface area of the samples. Comparison of the surface areas listed in *Table 1* with the titration curves shows that the extent of the deviation of the titration curves from the blank parallel the differences in surface area.

Structural Composition

A plausible and intriguing hypothesis for the chemical and structural composition of the surfaces of borosilicate glasses such as "E" glass, or "Pyrex", and of soda-lime or "soft" glasses can be constructed by combining the results with those of several published studies of the adsorption characteristics of such glass.

Some very interesting studies on the adsorption of various radioactive ions on "Pyrex", soda-lime, and fused silica glass surfaces were performed by James W. Hensley, et al (4, 5). Hensley found that approximately monolayer amounts of cations such as radioactive sodium, silver, and caesium were adsorbed rapidly on the glass surface. At room temperature, adsorption of greater than monolayer quantities did not occur. Above room temperature, multi-layer adsorption did occur, and at 90°C., penetration of the glass surface to about 5 atom layers deep can take place for strongly adsorbed ions such as radioactive sodium. Activation energies for this multilayer adsorption process are similar to those found for the migration of sodium ions in the bulk phase of glass.

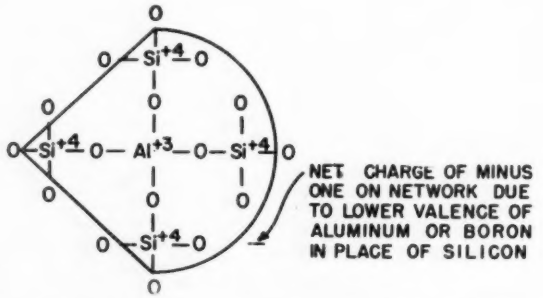


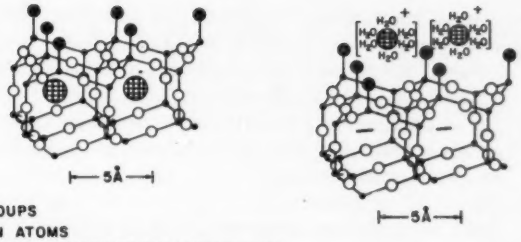
Figure 6. Effect of isomorphous substitution of aluminum or boron for silicon in silica tetrahedral lattice

A comparison of the adsorption of radioactive sodium ions on the surface of fused silica with that adsorbed on the glass surface showed significant differences between them. At a pH of about 8.6, only fractions of a monolayer were adsorbed, ranging from four hundredths of a monolayer at 30°C., to three thousandths at 69°C. These differences in fractional coverage, and the negative temperature coefficient for adsorption on a fused silica surface vs. the highly positive coefficient for adsorption found on glass (i.e., adsorption on the fused silica surface decreases tenfold with an increase in temperature, whereas that on glass increases five-fold), indicates that the surface of glass is fundamentally different from that of fused amorphous silica.

If the reasonable assumption is made that adsorption of cations such as sodium occurs only at negatively charged sites on the surface, these results and those of Hensley agree very well.

Titrations indicated that only weakly acidic silanol groups are present on the surface of pure silica glass. The fraction of such groups on the fused silica surface which would be negatively charged at the pH and neutral salt levels used by Hensley were calculated from equation (1). This calculation indicated that 0.05 of the surface groups should be ionized. This is in excellent agreement with the figure of 0.04 of a monolayer of adsorbed sodium ions found by Hensley. This agreement supports the hypothesis that cation adsorption takes place only at negatively charged surface sites.

The much higher cation adsorption on soda-lime and "Pyrex" (borosilicate) glasses found by Hensley is consistent with the relatively large number of strongly acidic sites having pKa values between 3 and 5 found in the titrations of complex glasses having similar composition to "Pyrex" (e.g., "E" glass and "alkali glass"). At all pH values above 5.0, these sites would be mostly negatively charged and almost full surface coverage by adsorbed cations might be expected. It seems quite reasonable that these acid sites are borosilicate and aluminosilicate groups formed by the isomorphous substitution of boron and aluminum ions into the tetrahedral lattice structure of the silica network. This type of substitution is illustrated in *Figure 6.*



● = OH GROUPS
○ = OXYGEN ATOMS
▪ = SILICON OR ISOMORPHOUSLY SUBSTITUTED BORON OR ALUMINUM ATOMS
⊕ = SODIUM CATIONS

Figure 7b. Hydration and partial ionization of surface alkali cations

Figure 7a. Schematic representation of a possible surface structure for "E" glass

Substitution of trivalent ions for quadrivalent silicon ions leaves a net negative charge on the lattice which must be compensated by cations such as Na^+, H^+, or 1/2 Ca^{++} to preserve electrical neutrality. Such groups are known to occur in the bulk phase of the glassy structure from X-ray and infrared studies of borosilicate and aluminosilicate glasses. They have also been found in the crystalline aluminosilicates, such as the clay acids (e.g., montmorillonite) in aluminosilicate cracking catalysts, and in inorganic ion exchange materials such as the zeolites, permutites, and ultramarines. Studies of montmorillonite clays by Marshall (6) and of the aluminosilicate cracking catalysts by Planck (7) have shown that such structures are indeed strongly acidic when compared to silanol groups and that they have (pKa) values of the order of 3 to 4. This is just the order of acidic strength indicated by the titrations of the glass surfaces here.

The number and types of acidic surface groups present on the glass surfaces studied are summarized in *Table 2*. The number of silanol groups per square millimicron of surface were computed by equation (4), using the cc. of base required to titrate from a pH of 7.5 to 9.25, in excess of that required to titrate a blank over the same pH range, as the measure of the base reacted with the surface silanol groups. This neglects the fraction of base bound below pH 7.5 by silanol groups, but calculations using equation (1) indicate that no serious error is introduced by this.

The number of more strongly acidic surface sites was calculated from the excess of base required to titrate between a pH of 2.5 and 7.5 for the sample titration over the blank. The formula used here was:

$$\frac{\text{strongly acidic sites}}{\text{square millimicrons}} = \frac{\text{moles of base/gram} \times 6 \times 10^{23}}{\text{SA} \times 10^{18}}$$

This formula assumes that these sites were completely titrated at a pH of 7.5. If titration is not complete at this pH, the number of strongly acidic surface groups will be underestimated by the above formula.

Table 2 also gives the number of water molecules per square millimicron of surface, computed by dividing the water evolved per gram on heating from 110° to 610°C. by the surface area in square millimicrons per gram. It will be noted that this hydration is very high and is several times larger than is physically reasonable for surface hydration alone.

A further study was made on heat-cleaned "E" glass cloth to determine the temperatures required, within the range of 110°C. to 610°C., to eliminate this water. About half of the total came off between 110°C. and 150°C., about one-fourth between 150°C. and 350°C., and the remaining one-fourth between 350°C. and 610°C. If the water evolved between 110°C. and 150°C. is assumed to be strongly physically bound, the remainder is about right for providing for the constitutional water bound as silanol groups and a hydration number between 6 and 12 for the counter-balancing cations required to neutralize the charges of the strongly acidic surface groups. (*Figure 7-b*)

The ratios of silanol to strongly acidic groups for "E" glass indicate a surface composition approaching that of an alkali aluminosilicate such as $NaAlSiO_4$. Structurally it may be similar to known crystalline compounds of this composition such as "Nepheline" (tridymite structure) or "Carnegiete" (crystobalite) structure.

Evidence that the structure and chemical composition of the glass surface may be unexpectedly simple and comprise only silanol groups, alumino or borosilicate groups, and *alkali* cations to counterbalance their negative charges, is furnished by Hensley's work on the adsorption of radioactive anions on soft glass and "Pyrex". Hensley found that anion adsorption, in contrast to cation adsorption, was almost completely negligible on fresh, heat-cleaned, soft (soda-lime) glasses, and on "Pyrex" (sodium, calcium, boroaluminosilicate) glasses. The amounts of radioactive bromine, carbonate and phosphate ions adsorbed were less than that corresponding to the coverage of one-one thousandth part of the surface with such ions.

Autoradiographic examination of glass samples exposed to radioactive phosphate solutions showed that strong adsorption of phosphate did occur, however, on all cracks, faults and imperfections which penetrated the glass surface and reached the interior of the glass structure.

Hensley also found that etching away the surface layers of these glasses in hot caustic solution exposed strong anion adsorption sites. Radioactive phosphate ions were adsorbed at these sites in amounts corresponding to a coverage of about 20% of the available surface. Acid leaching the surface exposed by etching in caustic solution caused an immediate loss of this anion exchange capacity. Periods of time as short as two minutes were sufficient to completely remove phosphate adsorption sites. It was also found that adsorption would not occur from solutions of phosphate ions having pH's lower than about 4, even in the absence of acid leaching. Phosphate adsorption could be induced either on fresh glass surfaces or on acid leached surfaces by a prior adsorption of zinc ions.

These results strongly suggest that the surface regions of soda-lime and "Pyrex" (borosilicate) glasses probably contain almost no polyvalent metal ions in octahedral configurations. This would include ions such as magnesium, calcium, aluminum (in octahedral coordination positions), iron, lead, zinc, titanium, etc.

In the previously cited work of C. J. Planck, (7) it was shown that the octahedrally coordinated aluminum ions in aluminum oxide strongly adsorb anions, particularly phosphates.

Hensley's work shows that surface adsorbed zinc ions also adsorb phosphate, and unpublished work by one of the authors of this article indicates strong adsorption of phosphate and other polyvalent anions on octahedrally coordinated magnesium ions in magnesium silicate minerals such as chrysotile asbestos.

The strong phosphate adsorption shown by soda-lime and "Pyrex" glasses where the surface layer has been removed by caustic etching shows that the octahedrally coordinated metal ions, such as calcium, present in the bulk phase, do adsorb phosphate. Since these sites are destroyed instantly by acid leaching, or even by immersion in solutions having a pH lower than 4, they cannot belong to the network structure of the glass. Since they persist down to a pH of 4, however, they are probably not sodium or potassium ions, which would likely be leached out of the glass surface before this relatively low pH was reached.

Corroborating evidence for the hypothesis that soft (soda-lime) glasses and borosilicate glasses have no polyvalent metal ions (i.e., calcium, magnesium, aluminum, titanium, zinc) held at the surface in octahedral configurations, is available from an entirely different type of experimental approach in some recent work reported by Anderson and Kimpton (8). These workers showed that a whole series of special glasses containing extremely large amounts of various types of polyvalent metal ions (calcium, titanium, bismuth, barium, lead) as well as pure crystalline oxides which contained such ions, adsorbed monolayer quantities of oxygen with extremely strong forces of adsorption. After having adsorbed this oxygen, neither the glasses nor the crystalline compounds were perfectly wetted with water. Soft glasses, borosilicate glasses, and quartz, however, did not exhibit this phenomena. In the special glasses studied by Anderson and Kimpton, the concentration of the polyvalent cations was so large that it would have been impossible to have completely coated the surface with silica tetrahedra or with boro- or alumino-silicate tetrahedra. Anderson and Kimpton give an interesting explanation for both the strong adsorption of oxygen and the poor wetting characteristics of the surface after the oxygen has been adsorbed.

They point out that surface oxygen octahedra may be expected to have one vacant oxygen site and consist of inverted pyramids with a square base in the surface. The metal ion is near the surface at the center of the oxygen square. Because of the asymmetrical force field, the metal ion is unable to hold an oxygen ion in position at a site which would be essentially above the plane of the surface, and yet associated with the metal ion in the oxygen vacancy is a potential wall of sufficient depth to adsorb an oxygen molecule with more than Van der Waal's force. The oxygen monolayer adsorbed at these active sites forms a protective film over the glass surface and prevents the formation of hydrogen bonds between the glass and possible wetting water. This implies that the monolayer is actually molecular oxygen, O_2.

In the case of fused silica or glasses in which the silica tetrahedron is the only coordination unit, there are no exposed metal ions at the surface, but rather the surface is all oxygen atoms. Similarly, in the case of boron oxygen triangles or borosilicate glasses like "Pyrex" brand glass, the boron ion is pulled completely below the surface by the asymmetrical field and leaves an oxygen triangle in the surface. Consequently, in neither case is there a possibility of an active center such as is proposed for the octahedra. Thus, these glasses are not expected to absorb oxygen and become hydrophobic. This was verified by their experiments.

Since both soft glasses and borosilicate glasses contain appreciable amounts of polyvalent metal ions which exist in the bulk phase of glass in octahedral configurations, the absence of such structures in the surface region appears to require an explanation. Weyl (9) has suggested that there is a strong tendency for highly-charged metal ions to screen their positive charge with the more polarizable oxygen ions when possible. He points out that this would give the surface configuration a lower surface energy. This explanation would account for the relatively low surface energy shown by those materials such as silica and boric oxide where complete screening of the positively charged polyvalent metal ions by the oxygen is possible structurally. This can not occur, however, for all glasses, as shown by the work of Anderson and Kimpton.

The authors believe that a possible explanation for the differences in surface and bulk phase compositions and structures may be that the lower surface energy constituents of a glass batch will concentrate in the surface region, and that all constituents of the batch present in the surface will adopt those configurations which minimize the surface energy to the greatest extent possible. Thus, alumina in the surface will probably adopt a configuration whereby it is substituted in the tetrahedral lattice rather than exist in an octahedral configuration. The surface energy can also be minimized by neutralizing the charges which are thus placed on the glass network with sodium ions or potassium ions rather than with polyvalent cations such as calcium or magnesium, which have much higher force fields. (Such an effect might also explain the positive temperature coefficient of surface tension which have frequently been observed for these types of glasses.) Such a preferential concentration of lower surface-tension constituents and configurations in the surface would probably be maximized in a glass spinning operation, since here the increase of surface energy would be very great without such a tendency.

It must be recognized, however, that this process represents a type of "demixing" of the glass constituents, and this is a counterbalancing thermodynamic term opposing concentration of lower surface energy constituents at the surface. That is, the free surface energy of the spun glass can be minimized by concentrating the lower surface energy constituents and configurations in the surface region, but this is done at the expense of a thermodynamically unfavorable (lower entropy) segre-

gation process. If the demixing process must be very extreme in order to allow the presence of only low energy structures at the surface, a purely low energy surface may not be attainable. The special glasses studied by Anderson and Kimpton probably represent such cases.

It is interesting to speculate, if the above explanation is correct, that glasses of special surface compositions could be obtained by the proper choice of constituents having low surface energies as a portion of the glass batch. Since water and hydroxyl ions have very low surface energies, if water is not completely eliminated from the glass batch during the melting operation, they may be expected to concentrate in the surface region and give a more highly hydrated surface than the bulk phase.

To summarize the discussion of the nature of the glass surface, it appears both from this work and that of others, that the surface of pure silica glasses contains only silanol groups which behave as polymeric weak acids. More complex glasses such as soda-lime, borosilicate, and aluminosilicate glasses have silanol surface groups, but, in addition, they also have relatively strongly acidic boro- and aluminosilicate surface structures formed by the isomorphous substitution of boron or aluminum in the tetrahedral lattice of silica. The net negative charges thus placed on the framework of the glass are compensated by alkali cations. Except for glasses of very unusual composition (i.e., very rich in polyvalent metal oxides other than SiO_2, B_2O_3 and Al_2O_3) or more common glasses which have been especially etched in hot caustic to remove the surface layer usually present, no polyvalent metal ions but those capable of acting as part of the silica tetrahedral lattice are present at the surface. The surface structure is sufficiently open in spots to allow the diffusion of sodium ions into the interior of the glass. The surface is likely more highly hydrated than a pure silica surface.

A pictorial representation of this concept of an "E" glass surface is shown in *Figure 7-a and 7-b.*

Nature of Chromium Complex Coupling Agents

Since many readers may not have had an occasion to study the chemistry of chromium compounds extensively, a brief review of some of its important aspects would be in order. This review is taken largely from a similar summary of the chemistry of chromium compounds by E. W. Merry (10) and by Udy (11). Some of the more important aspects of the chemistry of chromium compounds are as follows:

1. Trivalent chromium compounds have a central chromium atom linked by coordinate valences to six other molecules, groups, or ions, forming a chromium complex. This complex, according to the nature of the coordinated groups, may be neutral, or positively or negatively charged. The charged complex may be mono-, di-, or trivalent. The positively charged complexes form salts with anions of acids; the negatively charged complexes form salts with metallic (and other positively charged) ions. The six coordinated molecules or groups may be six water molecules. In this case, the complex is positively charged and trivalent. Negatively charged ions such as hydroxyl, chloride, or 1/2 sulfate, may penetrate the complex, displacing water molecules and reducing the positive charge. The introduction of three such groups into the complex gives it a neutral reaction. The introduction of four to six such groups gives it a negative charge.

2. Chromium salts hydrolyze in aqueous solution, giving basic salts and free acids. These basic salts contain hydroxyl ion in the complex.

3. Increasing the pH value of a chrome solution by adding alkali leads to increased hydrolysis, formation of basic salts, and penetration of hydroxyl ions into the complex. Lowering the pH of a chrome solution by adding acid reverses these changes.

4. The molecules of chromium salts containing water molecules and hydroxyl groups in the complex tend to become associated through the direct linking of a hydroxyl group already attached to one chromium atom, with a second chromium atom. In the formation of this linkage a molecule of water is eliminated. This process is known as "olation". Hydroxyl groups in the complex can be titrated directly by acid. Olated hydroxyl groups cannot be titrated directly by acid.

5. The addition of alkali, increase of temperature, or increase in the concentration of chromium, favors olation. The addition of acid, a decrease in temperature, or dilution, reverses olation. At equilibrium, under certain conditions 85 to 90% of the hydroxyl groups may have passed into the olated form.

6. Olation may link up two or more chromium atoms, leading to the formation of complexes of considerable size. Besides olation, polymerization can lead to an increase in particle size.

7. The groups, other than water, which become coordinated with the chromium atom in the complex, may be arranged in the following series: nitrate, chloride, sulfate, formate, acetate, and oxalate, tartrate, and hydroxyl. This series gives the order of the stability of binding in the complex, nitrate being the least stable, and oxalate, tartrate, and hydroxyl the most stable. Water probably comes between nitrate and chloride.

8. Neutral groups which can be coordinated by trivalent chromium include water, ammonia, SO_2, NO, NO_2, S, alcohols, PH_3, N_2H_4, etc.

9. The rate of exchange of coordinating groups in the coordination sphere of a chromium complex is a relatively slow process. This is thought to be due to the fact that in the octahedral binding of chromium with six coordinating molecules, a d^2sp^3 set of orbitals of the chromium atom are used. This leaves only three "d" orbitals available, each one of which is filled with a single electron.

The process of exchange of coordinating groups in complex ions of transition metals usually involves a temporary expansion of the coordination number using an unfilled "d" orbital in the formation of the transition complex. When such unfilled orbitals are available, the transition complex is at only a slightly higher energy level than the starting complex, or the end product; activation energies are low, and exchange reactions are rapid. When no unfilled "d" orbitals are available (as in the case of chromium), the transition complex containing seven coordinated groups can only be formed by pairing the electrons in one of the singly occupied orbitals and thus freeing another one for the

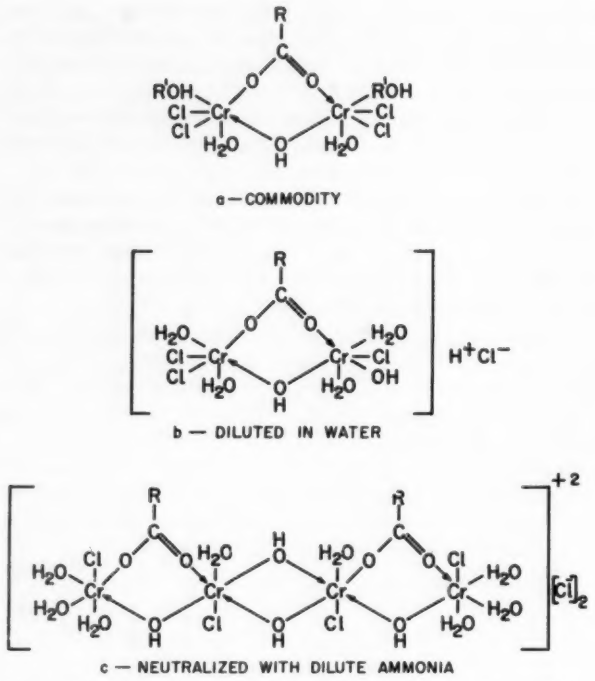


Figure 8. Structure of "Volan" molecules during solution preparation steps

formation of the transition complex. The transition complex in such a case lies at a much higher energy level than the starting complex, or the product in which the replacement of ligands has occurred. The activation energy is quite high, and the rate of replacement is low.

10. There is considerable evidence that carboxyl groups can function as bridging agents between two or more chromium atoms in the same fashion that hydroxyl groups do in the olated chromium compounds. There is also evidence that both carboxyl type bridging and olation can occur in the same compounds.

From the above summary, it should be evident that the chemistry of the chromium complex coupling agents used in fiberglass laminates is likely to be quite complicated.

When used commercially, a typical such complex, "Volan" methacrylato chromic chloride (a product of E. I. du Pont de Nemours & Co., Inc.) is supplied as a material with the structure indicated in *Figure 8-a*. Upon dilution with water from its largely organic medium, some hydrolysis occurs immediately, and a portion of the chloride which is coordinatively bound is replaced by hydroxyl groups taken from the aqueous solution. This type of change is schematically depicted in *Figure 8-b*.

Upon being neutralized to a pH of 6 with ammonia, more of the chloride ions are displaced from the coordination sphere by hydroxyls coming from the ammonium hydroxide. The chrome complex at this point has a sufficient number of hydroxyl groups to begin the process of olation. (*Figure 8-c.*)

As olation proceeds, the complex increases in molecular size, and the charge inside the complex also increases. For example, the total charge on a dimer may be +4, on a trimer +6, etc. The coordinated water

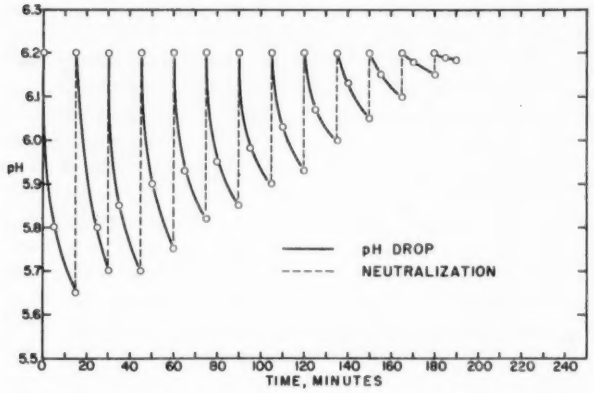


Figure 9a. Repeated neutralization of 2% "Volan" solution with 1% NH_3 solution

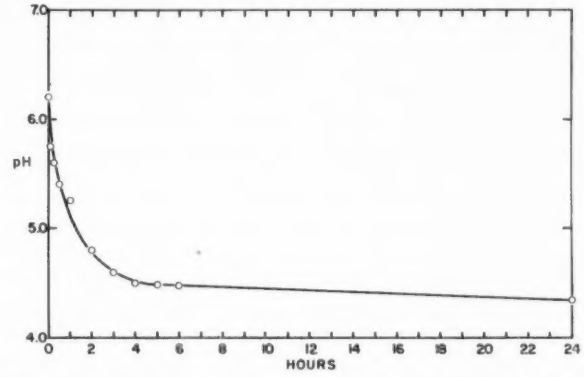


Figure 9b. pH drop vs time for neutralized 2% "Volan" solution

molecules are close, not only to the charged chromium atom with which they are coordinated, but to a second or third chromium atom linked to theirs by olation. The high positive charge causes the water molecules to become more strongly acidic, and a proton is expelled from one of them. This leaves the coordination sphere along with a chloride ion, forming HCl, which causes the pH to decrease.

Thus the pH of a freshly neutralized solution of "Volan" does not remain constant, but decreases steadily as the processes of olation and further hydrolysis occur. This process will rapidly decrease in rate, since the process of olation is opposed by a lower pH. If the complex is readjusted to a pH of 6 with additional ammonium hydroxide, the same process occurs a second time, but the asymptotic leveling out takes place at a slightly higher pH. The sequence of neutralization, aging to allow olation and hydrolysis to take place, and reneutralization, can be repeated many times. This is shown in *Figure 9-a*. *Figure 9-b* shows the rapid initial decrease of pH and its asymptotic leveling out as a function of time for a particular neutralization.

When a sample has been neutralized and aged many times, it is finally possible to obtain a substantially chloride-free material (i.e., there is no longer any chloride in the coordination sphere of the chromium). In such "polyneutralized" products, olation has proceeded to a significant degree. The probable structure of such a material is shown in *Figure 10*.

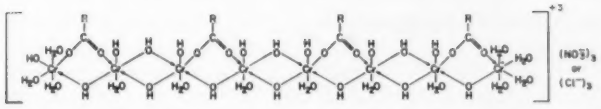


Figure 10. Structure of polyneutralized chromium complex

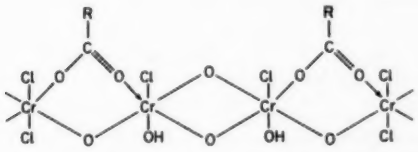


Figure 11. Structure of dried "Volan" commodity

It should be understood that the above description is thought to be generally correct, and it will be supported by evidence, but the particular structures shown undoubtedly represent an oversimplification of the actual situation. From the description of the large numbers of different types of materials which can coordinate with chromium, and in consideration of the fact that both olation and polymerization can occur, it should be evident that many species other than those given structures probably exist.

Some of the changes described have been followed by analytical techniques involving drying the chromium complex at a low enough temperature that only the excess solvent is eliminated. This was done on the "Volan" starting commodity over a period of 3 weeks at 50°C. in a drying oven. As shown in *Table 3*, the analysis corresponded quite closely with that expected from the formula of *Figure 8-a*.

Table 3. Dried "Volan"

	Commodity		Neutralized 2% Solution	
Drying Temperatures	**50°C.**	**150°C.**	**50°C.**	**150°C.**
CHEMICAL ANALYSES				
% Chromium	19.06	26.89	19.2	26.0
% Chloride	27.4	33.40	29.4	29.8
% H_2O	26.6	3.05	17.0	7.3
% Carbon	37.49	14.62	9.40	9.38
% Nitrogen	—	—	6.97	4.98
Bromine number	300	161	—	—
MOLES PER 100 GMS.				
Chromium	0.366	0.517	0.369	0.500
Chloride	0.773	0.942	0.828	0.839
H_2O	1.478	0.169	0.944	0.406
Methacrylic acid	0.188	0.305[1]	0.196[1]	0.195[1]
Isopropanol	0.79	—	—	—
Free chloride[2]	—	—	0.330	0.483
MOLE RATIOS				
Cl/Cr	2.11	1.50	0.89	0.97
Methacrylic acid/Cr	0.51	0.59	0.53	0.39
H_2O/Cr	4.04	0.33	2.56	0.81
Isopropanol/Cr	2.16	—	—	—

[1] All carbon assumed to be in the form of methacrylic acid with some polymerization of double bonds due to high temperature.
[2] Corrected for chloride held as NH_4Cl.

When further dried at 150°C. (the usual drying temperature after application on a glass surface), virtually all of the coordinated water molecules and other solvent molecules such as isopropanol are driven off, and only the methacrylic acid, some chloride, oxygen, and a small amount of water in the form of hydroxyl groups remain. The chemical composition is given in *Table 3* and a reasonable probable structure for it is given in *Figure 11*.

An interesting point is that the methacrylic acid has copolymerized with itself to a certain degree, as a result of this treatment. The number of double bonds titratable by bromine is only about half as much as the coordinated acid. This indicates that methacrylic acid attached to chromium can undergo a vinyl-type polymerization with itself.

A similar analysis of low and high temperature-dried "Volan" complex after it has been diluted with water and neutralized according to the recommended industrial procedure is also given in *Table 3*, and its probable structure indicated in *Figure 12*. It will be noted that there has been a partial displacement of some of the chloride from the coordination sphere as a result of this process.

It is possible to obtain information about the changes taking place as the complex is diluted and neutralized by solvent extraction procedures. Aqueous solutions of the complex can be mixed with secondary butanol and an organic-rich phase then salted out by saturating the resulting solution with sodium chloride or sodium nitrate. The complex distributes itself between the aqueous and the organic phase. When sodium nitrate is used as the salting out agent, it is possible to analyze for the ratio of chromium to chloride in the organic phase and for the ratio of methacrylic acid to chromium in this phase, and thus obtain some information about the changes taking place after hydrolysis and neutralization.

It has been found by this technique that the methacrylic acid is always associated with the chromium. In those cases where all chromium is extracted into the organic phase, no methacrylic acid remains in the aqueous phase. It was also found that ammonium chloride was not extracted into the organic phase under these conditions.

Studies are available in the literature of the extractability of a wide range of transition metal salts into organic solvents which have shown that nitrates are generally much more highly extracted than are chlorides. This is particularly true of those compounds in which the bonding is essentially ionic.

Since these experiments indicate the nitrate salt was present in a huge excess with respect to chloride, it seems reasonable that any ionic chloride would have been displaced by nitrate in the material found in the extracted phase. The ratio of chlorine to chromium should then be a measure of how much chlorine was coordinatively bound to the chromium.

Table 4 shows the amount of chlorine found per chromium atom for the freshly diluted complex which had not been neutralized, the complex which has been neutralized to a pH of 6, and for the polyneutralized

Table 4. Solvent Extraction of "Volan" Solutions

2% "Volan" Solution	WATER PHASE			SOLVENT PHASE					
				Soluble Portion			Insoluble Portion		
	Chloride/ Chromium Ratio	% of Total Chrom.	% of Total Chlor.	Cl/Cr Ratio	% Total Chrom.	% Total Chlor.	Cl/Cr Ratio	% Total Chrom.	% Total Chlor.
Unneutralized	—	51	—	—	49	—	No insoluble portion		
Neutralized to pH of 6.2	7	37	85	0.46	42	6	1.3	21	9
Polyneutralized at pH of 6.2	53	4	98	5	0.5	1	0.03	96	1

material. There is a good correspondence between the amount of chloride remaining associated with the complex after drying at 150°C. and that which is coordinatively bound, as shown by the extraction studies. It is also noteworthy that substantially no chloride appears to be coordinatively bound in the polyneutralized material.

There were at least two distinct species which could be extracted. One of these was found to be the sole species present in the unneutralized complex, and the predominant species present in non-aged complex neutralized to a pH of 6. (*Figure 8-b.*)

The second species, which has a much higher partition coefficient for the organic phase than does the first, makes its initial appearance in the material which has been neutralized to a pH of 6, and is the sole constituent of the polyneutralized material. (*Figure 10*)

These two phases are distinguishable, in that the one which still contains chloride in the coordination sphere remains in solution after extraction into the organic phase, whereas the more highly olated and substantially chloride-free material flocculates out and becomes insoluble after aging for about 24 hours in the organic phase. This may be due to the continuation of the process of polymerization, which leads ultimately to the formation of products of sufficient size that they are no longer soluble in the organic medium.

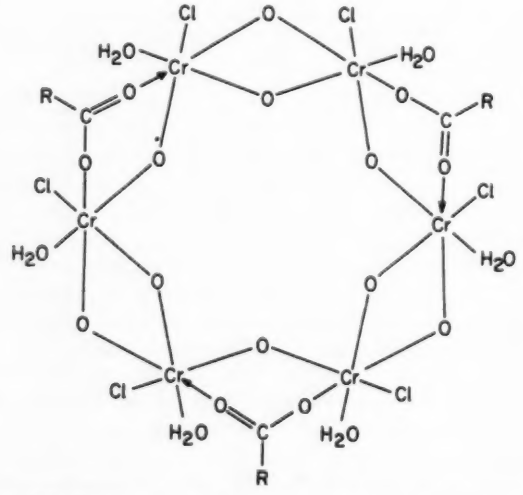


Figure 12. Structure of "Volan" dried from neutralized 2% solution

Interaction of the Coupling Agent with the Glass Surface

The usual commercial practice involved in applying a coupling agent is a dry-down procedure, wherein the glass cloth, fiber, roving, etc., is saturated with the aqueous treating solution and is then dried. Analysis of glass treated in this manner cannot give meaningful information about the fundamental nature of the interactions between the glass surface and the coupling agent, since the chrome or other coupling agent found on the surface is a mixture of that which is chemically bonded to the glass, and that which was merely deposited as an excess from the trapped solution when it was dried. To study the interactions which were due solely to chemical bonding between the glass and the coupling agent, has involved treating the substrate with the treating solution, and thoroughly washing it to get rid of all material other than that which is sufficiently strongly chemically bound that it cannot be displaced by wash water.

First, studies were performed on pure amorphous silica having a high surface area. This was chosen since it is a material of very well characterized chemical composition and surface structure, and is quite pure. The material used ("Ludox" Colloidal Silica, a product of E. I. du Pont de Nemours & Co., Inc.) was deionized in a mixed bed ion exchange resin, and oven-dried at 110°C. to give a product having a specific surface area of 190 to 200 m^2/g.

Previous work had shown that such a material has about eight silanol groups per square millimicron on its surface and substantially no other groups. If this surface is exposed to moist air, a monolayer of strongly adsorbed water is rapidly picked up on its surface, and if the relative humidity is sufficiently high, additional layers of relatively weakly-bound, physically-adsorbed water are also picked up. A study of the interaction of the coupling agent with a pure silanol surface was desirable to show the types of interactions which can be expected from this part of the complex surface of fiberglass. Knowing this, the additional interactions which are then found to occur on actual fiberglass surfaces can likely be attributed to the borosilicate and aluminosilicate surface groups.

Figure 13 shows the amount of chromium picked up on the amorphous silica surface as a function of the pH of the treating solution. For comparison, *Figure 13* also shows the average molecular weight of chromium complexes formed in basic chromic chloride, nitrate, and sulfate solutions as a function of pH. The latter data were taken from the literature. Molecular weights were

determined by measurement of changes in the diffusion coefficients of these three materials as a function of pH or their degree of neutralization. The work on basic chromium nitrates was done by Jander and Scheele in 1932, and that on the basic chromium chlorides and sulfates, as well as a recheck of the nitrate results done by Riess and Barth in 1935 (10).

It will be noted that there is a striking agreement in the general appearances of the curves for the change in the percent chromium picked up on the amorphous silica surface as a function of pH and the change in the average degree of polymerization or number of chromium atoms per molecule in the basic chromium salts.

It should be recalled, however, that the number of charges on the amorphous silica surface (or the number of ionized sites) is also a sensitively changing function of the pH, and neutral salt content.

Figure 14 shows the number of negatively charged sites available on the amorphous silica surface, plotted against the number of chromium atoms retained on the surface.

It will be noted that up to a pH of about 5, only one, or at the most, two, chromium atoms are picked up at each charge site on the silica surface.

Above this pH, in the same region where the molecular weight studies indicate a rapid increase in the degree of polymerization of the chromium atoms, an average of about eight chromium atoms are picked up for each newly available charged site on the silica surface. The overall chromium pickup corresponds to an average curve between the two curves shown in *Figure 14*, which would be obtained by drawing a straight line from the origin to the experimental point.

This indicates that when the complex used in treating has a pH below 5, low molecular weight chromium species similar in structure to those shown in *Figures 8-a and 8-b* are the only ones present in appreciable quantities, and these occupy all of the negative sites available on the silica surface. At pH's above 5, however, the treating solution contains both low and high molecular weight species, depending on the exact amount of neutralization and the extent of aging, and both of these types of species compete for sites on the silanol surface with the competition strongly favoring the polymerized species as the pH of the solution is further increased.

An interesting sidelight of the study of the effect of chrome pick-up on the treated and dried amorphous silica surface is that the water picked up by adsorption decreases as the amount of chromium pickup on the surface increases. (*Figure 15.*) This is somewhat surprising, since the amount of chromium picked up is at all times far insufficient to coat the whole surface. It may be that the chromium complex masks negatively charged sites which would otherwise serve as initial nucleation points for water adsorption, or perhaps it functions by adsorbing oxygen and creating hydrophobic spots on the surface, as suggested by Anderson and Kimpton.

The information obtained on the silanol surface studies appears to apply quite satisfactorily to the glass surfaces also. Here, however, since there are strong acid sites (boro- and alumino-silicate) on the glass surface which are ionized and thus negatively charged at all pH's studied, the amount of chromium picked up and chemically bonded to the surface is much higher per unit surface area than was found for silica. There is still a very good correspondence between the calculated num-

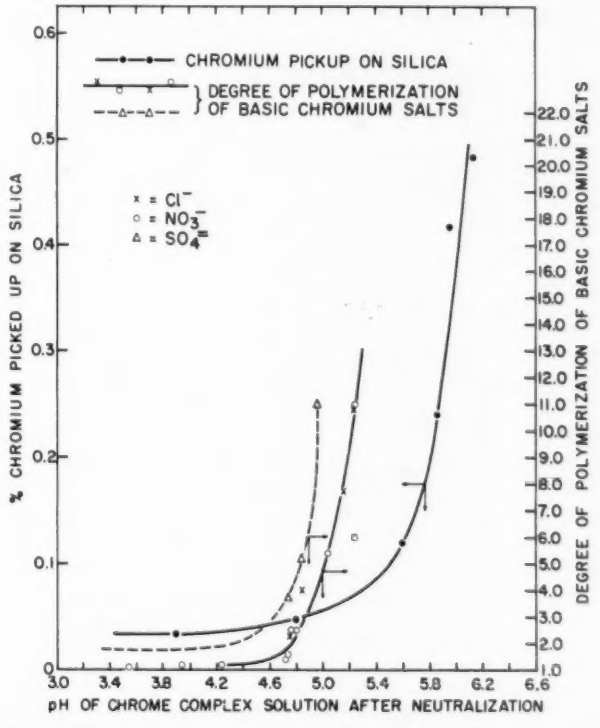

CHROMIUM PICKUP ON SILICA
DEGREE OF POLYMERIZATION OF BASIC CHROMIUM SALTS
x = Cl⁻
○ = NO₃⁻
△ = SO₄⁼
% CHROMIUM PICKED UP ON SILICA
DEGREE OF POLYMERIZATION OF BASIC CHROMIUM SALTS
pH OF CHROME COMPLEX SOLUTION AFTER NEUTRALIZATION

Figure 13. Chromium pickup on silica and degree of polymerization of basic chromium salt solutions vs pH of solutions

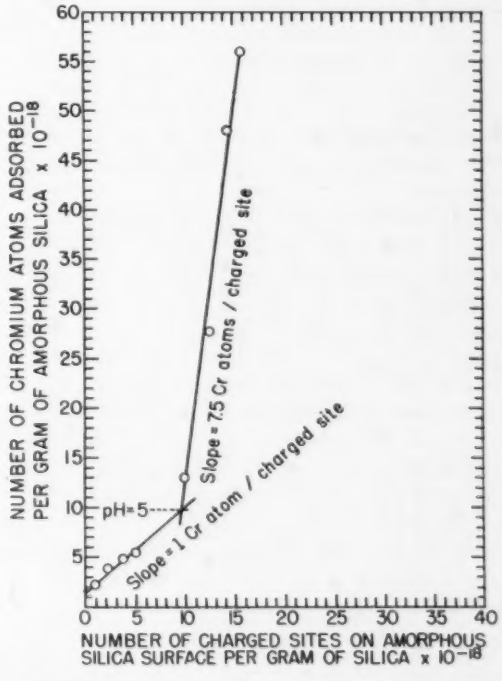

NUMBER OF CHROMIUM ATOMS ADSORBED PER GRAM OF AMORPHOUS SILICA x 10⁻¹⁸
pH=5
Slope = 7.5 Cr atoms / charged site
Slope = 1 Cr atom / charged site
NUMBER OF CHARGED SITES ON AMORPHOUS SILICA SURFACE PER GRAM OF SILICA x 10⁻¹⁸

Figure 14. Pickup of chromium complexes on charged sites on the surface of amorphous silica

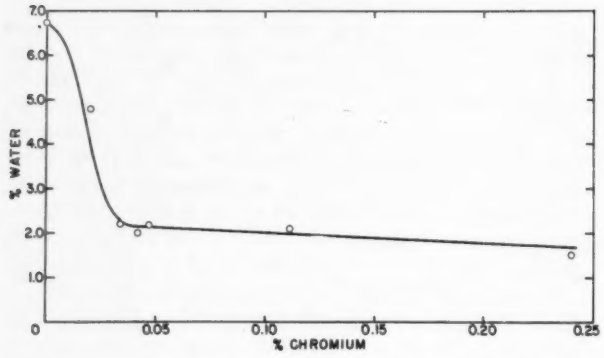


Figure 15. Water content vs chromium pick-up on silica

ber of negative charges as determined from the glass titration curves and the chromium picked up. Again, the amount of chromium picked up per unit negative charge increases with higher pH's, and with aging, indicating the pick-up polymeric chromium species. (*Table 5.*)

Summarizing the interactions of the chromium complex coupling agents with the glass surfaces, then, there seems to be fairly good evidence that a chromium complex molecule is adsorbed at each negatively charged site on the glass surface. As the pH is increased, or as the chromium complex solution is aged following neutralization, it polymerizes by a process of olation and the total chromium pick-up is increased. This indicates that the polymerized chromium is probably attached only at one site on the glass surface, at least initially. The pick-up of chromium on the surface changes the adsorption characteristics of the surface toward water vapor, decreasing it substantially even when the surface is not completely coated with chromium. Depending upon application conditions, such as pH, temperature, and aging, the nature of the chromium species adsorbed on the glass surface may vary from relatively low molecular weight species containing substantial amounts of chloride ions still in the coordination sphere of the chromium, to fairly high molecular weight species which contain substantially no coordinated chloride.

Ionically held chloride appears to be eliminated as HCl upon drying at a temperature of 150°C., but coordinatively held chloride is not. Most of the coordinated solvent molecules such as water, and organic solvents like isopropanol, are also eliminated by this drying.

Interaction of the "Volan"-Treated Glass Surfaces with Laminating Resins

Specific information on the types of interactions occurring between the "Volan"-treated glass surface and various laminating resins is both less extensive and more difficult to obtain than it was for the subjects previously covered. Most of the information is obtained by reasoning from analogy, rather than directly.

Commercial laminating resins are extremely complex in themselves, and the nature and number of reactive functional groups in them are seldom known with precision or certainty. There is also an extremely wide range of potential types of reactions which can occur between chromium complexes and such resins. In the

Table 5. Relationship Between Negatively Charged Sites on Various Glass Surfaces, pH, and Chromium Pickup

Treatment Code	Application pH	% Cr on Glass	Moles Cr per gram	Moles Negatively charged surface sites/g. at appln. pH (calculated from glass titration curves)	Chromium atoms picked up for each negative surface site
"E" GLASS CLOTH					
B	3.65	.0062	1.19×10^{-6}	1×10^{-6}	1.2
C	4.9	.0044	$.845 \times 10^{-6}$	1.2×10^{-6}	0.7
D	4.9	.0092	1.77×10^{-6}	1.2×10^{-6}	1.5
F	5.85	.009	1.73×10^{-6}	1.4×10^{-6}	1.2
E	6.40	.026	5×10^{-6}	1.5×10^{-6}	3.3
"E" GLASS FLAKES					
C	4.3	.0057	1.10×10^{-6}	4.7×10^{-6}	0.2
B	4.4	.0058	1.11×10^{-6}	5.3×10^{-6}	0.2
D	5.4	.017	3.27×10^{-6}	8×10^{-6}	0.4
F	6.1	.016	3.08×10^{-6}	13.3×10^{-6}	0.2
"ALKALI" GLASS					
B	3.55	.001	1.9×10^{-7}	Too small to measure	—
C	4.4	.002	3.8×10^{-7}	3.3×10^{-7}	1.2
D	5.3	.005	0.96×10^{-6}	1.5×10^{-6}	0.6
F	5.55	.038	7.3×10^{-6}	1.7×10^{-6}	4.3
"MICROFIBERS"					
B	3.95	.014	2.7×10^{-6}	9×10^{-6}	0.3
C	4.4	.075	14.4×10^{-6}	10×10^{-6}	1.4
D	5.3	0.11	21.2×10^{-6}	13.3×10^{-6}	1.6
F	5.75	0.14	27×10^{-6}	16.7×10^{-6}	1.5

summary of the chemistry of chromium complexes, it was pointed out that a wide variety of acidic, basic, and neutral organic groups were capable of forming coordinate complex bonds with the central chromium atom. In addition, "Volan" has a chemically reactive double bond in the methacrylic acid molecule attached to the chromium. Beyond this, studies of the chemistry of chromium complexes used in leather tanning have shown that they can undergo a wide variety of hydrogen-bonding reactions with most polar groups.

The most important types of chemical reactions occurring between the resins and the complex are likely to be:

a. Coordinate covalent bonding between carboxyl, alcohol, and amine end groups.

b. Reactions between Cr-Cl and CrOH groups with alcohol end groups to form Cr-O-R linkages with the elimination of either HCl or H_2O.

c. Copolymerization between the double bonds of methacrylic acid and reactive vinyl type double bonds in the resin.

Since the extent of this latter type of interaction, that is, the copolymerization of double bonds, has in the past been a question of some speculation, attempts to resolve it by two types of experiments were made. In one, the chromium complex with a polyester resin were copolymerized directly,* and then attempts to extract the complex and the resin with a solvent were made. It was found that the resin could be separated into three different phases by solvent extraction with acetone. One of these was a soluble component, a second was a resin phase which, although insoluble, was highly swollen, and the third was a strongly crosslinked, insoluble, and non-swollen resinous phase. These were each analyzed for their chromium content. It was found that the chromium was associated only with the two insoluble (and thus probably highly polymerized) fractions. Chromium complexes exposed to the same heat conditions as used in the curing were found to be still soluble in the extracting acetone solvent. It thus appears that some type of interaction capable of insolubilizing the complex had occurred between the complex and the resin. It further appears that the chromium was preferentially associated with the more highly polymerized fraction of the resin.

An indication that this experiment did involve the participation of double bonds, at least in part, is given by contrasting the strength of fiberglass resin laminates treated with the chromium complex of isobutyric acid vs those with methacrylic acid. Since these acids are identical except for the presence of the double bond in the methacrylic acid, any significant difference in their effectiveness as coupling agents should directly reflect participation of the double bond. It was found that the isobutyric acid complex gave laminates** whose strength after boiling was almost exactly halfway between the strength of control laminates containing no complex, and those made with the methacrylic acid. This appears to be fairly conclusive evidence pointing toward the participation of the double bond of the methacrylic acid in the bonding of the resin to a "Volan"-treated glass surface.

* A general-purpose, medium-reactivity polyester resin catalyzed with a 2% mixture of 50% benzoyl peroxide and 50% tricresyl phosphate, cured for 30 minutes at 121°C.

The Effect of Application Variables and Different Types of Chromium Complexes on Laminate Strength

When using a specific type of chromium complex as a coupling agent, it is still possible to vary the nature and amount of coupling agent present on the glass surface by several methods. The complex may be deposited by dry-down or substantively, from solutions of various pH values, and by aging and neutralizing to differing extents, in various stages of "olation" and polymerization.

There is a general tendency for the strength of laminates (after boiling) to increase as the chromium content on the glass is increased. This is true for application by dry-down which puts both chemically bonded and physically deposited chromium complexes on the glass surface. (*Figure 16.*) It is also true when only chemically bonded chromium is present on the surface, as in a glass which has been treated and thoroughly rinsed in water at room temperatures prior to drying. (*Figure 17.*) In both cases, the changes in the amount of chromium picked up were achieved by varying the pH of the solution.

It is very interesting to note that although the chemically bonded chromium comprises only 25%, or less, of the total chromium deposited by dry-down, it accounts for more than 75% of the difference in strength between controls containing no coupling agent and the samples treated by dry-down. This indicates that the chemically bonded chromium is about ten times as effective a coupling agent as that held physically per unit amount of chromium deposited.

It will also be noted that *Figures 16 and 17* each contain two sets of lines, with the upper one lying about 6000 psi above the lower. The upper line in each case was obtained from samples which had been aged after neutralization. These results indicate that the more highly olated and polymerized complexes are the most effective coupling agents. The most effective coupling agent in each case appears to be the polyneutralized material, in which the processes of olation and polymerization have probably proceeded to their ultimate extent.

A further indication that the polymerized complex is differentiatable in its action from monomeric, or low-polymer species is shown by the following experiment which was devised by R. K. Iler of this laboratory.

Dr. Iler has been studying the factors which influence the interaction between positively and negatively charged colloidal monolayers, and the interaction of such monolayers with positively and negatively charged ions and organic polymers.

He has been able to show that low molecular weight, positively-charged materials which are substantively held on a glass surface are not capable of functioning as bridges to hold negatively-charged particles to such glass

** A general-purpose, medium-reactivity polyester resin and "E" glass Style 181 batch heat cleaned glass fabric with a laboratory-applied finish, laid up in twelve plies and molded to stops to 0.125" thickness. The resin was catalyzed with a 2% mixture of 50% benzoyl peroxide and 50% tricresyl phosphate. The layup with the visible voids rolled out was inserted in a cold cavity type mold, heated from room temperature to 120°C over a one-hour period. Laminates contained about 60% by weight glass.

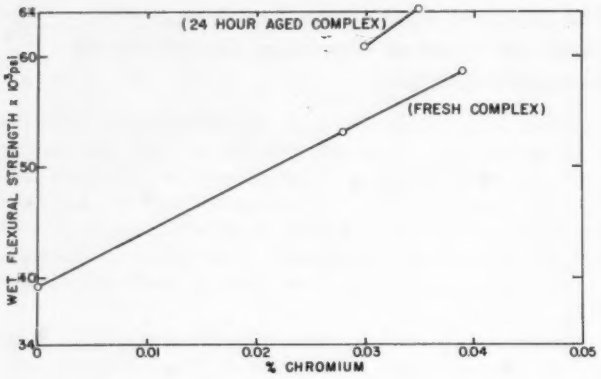


Figure 16. Wet flexural strength vs chromium content on glass cloth in glass reinforced polyester laminates (drydown method)

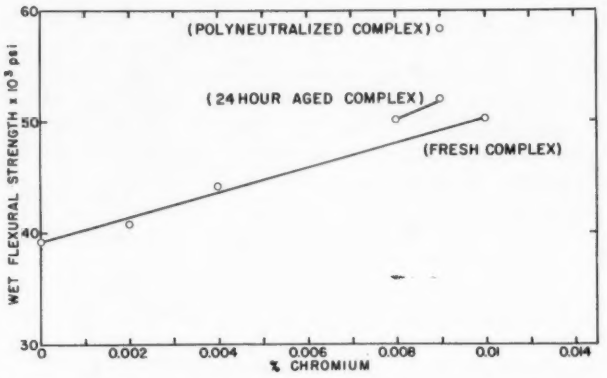


Figure 17. Wet flexural strength vs chromium content on glass cloth in glass reinforced polyester laminates (substantive method)

surfaces, if the charge on the glass surface and on the negatively charged colloidal particles to be deposited is sufficiently high.

In general, the degree of negative charge on a glass surface, or on some other negatively-charged surface decreases as a function of the pH of the solution from which deposition is performed. This is because most negatively charged materials contain acidic groups of one type or another in the surface, which are the cause of the negative charge. Since these acidic groups are often fairly weak acids compared, for example, to hydrochloric or sulfuric acids, lowering the pH will often cause them to exist in their non-ionic, proton-containing form, and thus lower their charge.

Dr. Iler showed that substantively deposited "Volan" which had not been aged to allow olation to proceed, would not hold negatively charged, 100-millimicron silica colloidal particles on the surface of a black glass plate at a pH of 7. At this pH, both the silica particles and the glass surface have a fairly high negative charge.

By contrast, polyneutralized "Volan" which had been aged and neutralized, until no further pH changes occurred, was an excellent mordant and was capable of functioning as a bond between the silica sol and the glass surface, even though both were negatively charged.

At pH 3, where the charge on the glass surface is greatly reduced, and there is substantially no negative charge left on the silica sol, *both* the low molecular weight and the polyneutralized "Volan" were excellent mordanting agents.

A = AREA TREATED WITH LOW MOLECULAR WEIGHT COMPLEX

B = AREA TREATED WITH POLYNEUTRALIZED HIGH MOLECULAR WEIGHT COMPLEX

Figure 18. Variation in the bonding of 100 millimicron colloidal silica to a glass surface by low and high molecular weight chromium complexes

The 100 millimicron silica sol used in this experiment was used merely as a representative of a board class of negatively charged materials, and has the advantage that a monomolecular film is visible because it shows interference colors on a smooth black glass surface. Any 100-150 mμ uniform sized negative colloid should work.

Figure 18 shows the result of this experiment. The area on the upper half of a black glass plate was treated in one section with low molecular weight "Volan", and in the other with polyneutralized "Volan" and the excess washed off. This was immediately washed and dried, and 100 millimicron silica sol poured over the surface and the excess sol rinsed off. It will be noted that only the area treated with the polyneutralized "Volan" appears shadowed, showing a pick-up of colloidal silica. This treatment was done at a pH of 7. The lower half of the black glass plate was then treated with 100 millimicron silica sol, the pH of which had been adjusted to 3, in exactly the same manner as described above. Here it will be noted that both of the "Volan" treated areas picked up appreciable amounts of colloidal silica, as shown by the very darkened appearance due to light scattering of the colloidal silica monolayer.

Since many organic polymers are negatively charged and have been found to behave in an analogous fashion to the negatively charged silica sol in this test, there does appear to be direct evidence that a highly polymerized chromium complex is more effective than a low polymer in at least this type of primarily electrostatic bonding of a negatively charged material to a negatively charged surface.

Finally, it should be noted that no single chromium complex is optimum for bonding to all types of resins. Whereas "Volan" is highly effective in bonding to polyester resins and to many other types, a recently developed chromium complex has been found to be greatly superior to "Volan" in bonding to epoxy resins. One of the major differences of this complex from "Volan" is the coordinating organic acid used. The rate of loss of strength of laminates* bonded with these two coupling

* Epoxy resin formulation: 100 parts diglycidyl ether of bisphenol A — 14 parts metaphenylene diamine. Layup at 55°C and rolled to remove voids as with polyester. Inserted into hot mold cavity (110°C). Closed to stops to 0.125" thickness and cured for one hour at 110°C. Laminates are about 60% glass by weight.

agents is contrasted in the extended boil test data shown in *Figure 19*. The great superiority of the new complex is quite evident.

Incidentally, it has been found that extended boil tests of this nature are necessary in the case of epoxy resin laminates to correlate meaningfully with field experience. Boil times which are satisfactory for polyesters show little difference between coupling agents which differ greatly in actual use situations.

In summary of this section, it appears that the amount of chromium picked up, the nature of its bonding to the glass surface, its degree of polymerization, the type of organic moiety attached to it, and the kind of laminating resins used, are all significant variables in determining laminate strength and its resistance to boiling water.

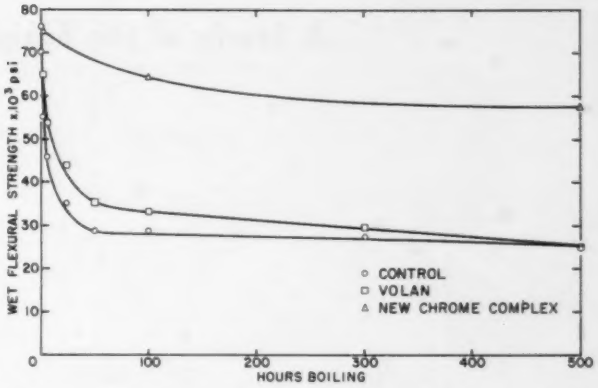


Figure 19. Loss of strength of epoxy laminates due to long term boiling

Conclusions

Although the surface of glass is complex, aluminum-boro-silicate glasses such as "E" glass may be considered to have weakly acidic sites in the form of SiOH groups and an approximately equal number of more strongly acidic sites caused by the isomorphous replacement of silicon atoms in the glass structure by boron or aluminum atoms. At pH values in the range of 3.0-6.0, only the more strongly acidic groups will be ionized to any appreciable extent. Titration studies, coupled with studies of surfaces, have shown that a chromium complex coupling agent molecule is chemically adsorbed from aqueous solution onto every negatively charged site on the glass surface. Thus, chemically adsorbed chromium complexes are largely adsorbed at the strongly acidic boro- and alumino-silicate sites in the 3.0-6.0 pH range and less at silanol sites, since only a small fraction of the silanol groups are negatively charged (ionized) in this pH range.

Comparison of the strengths after boiling of "E" glass cloth reinforced laminates finished with "Volan" finishes have shown that the improvement in strength over controls having no finished agent is largely derived from these chemically adsorbed molecules. Stronger laminates can be obtained by two general techniques. The first is to maximize the amount of chemically adsorbed chromium by applying the complex at the highest feasible pH. The second is to use the complex in a polymerized form. This can be done by repeated neutralizations and aging in a pH range of 5.9-6.2. The superiority of polymerized finishes over monomeric ones may be due to the development of a number of sites of attachment for each polymer molecule to the surface.

It appears that an acetone-insoluble and nonswelling phase forms on the surface of the "Volan" on curing a polyester resin to that surface. Since chromium structural complex without unsaturation gave distinctly inferior laminate strength retention during boiling, it may be inferred that there is a strong bond between the chromium complex and the polyester resin, and that the reaction of the unsaturation forms at least a part of this bond.

Although epoxy resins appear to bond well to "Volan"-finished glass, another chrome complex with an epoxy-reactive organic acid group has been developed that bonds in a more water-resistant manner to this resin than does "Volan". Since other glasses, including the high beryllia, high-modulus type and pure silica glasses, have distinctly different structural surface formulations from "E" glass, modified techniques for applying coupling agents to such glasses may be required to achieve optimum strengths.

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A Study of the Finish Mechanism:

Glass to Finish, Finish Thickness and Finish to Resin

A report of the work done under government contract for the purposes of—

a) supplying a test method for evaluating the ingredients used in a glass strand-resin structure

b) studying the factors needed to increase the strength and modulus of continuous filament wound structures

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To obtain highest physical properties in a resin-bonded glass strand structure, it is necessary that the individual glass filaments composing each strand be parallel, equally tensioned, and packed as close together as possible. Secondly, the glass-resin interface area must be studied to find the essential parameters that affect the stress transfer across this interface as the load is applied from the resin with its low modulus and relatively high deflection to the glass with its high modulus and low deflection. As the glass content increases, the filament cylinders are closer together and the critical shear area moves closer to the glass surface, increasing the relative importance of the resin-finish and finish-glass bond, and decreasing the importance of resin cohesive properties. As our work proceeded, we found that all failures in flexure occurred as an initial shear break on or adjacent to a filament interface. The purpose of this article is to present the results of this study of the resin-finish glass interface at 85% glass content by weight and the governing parameters determined to date, October 15, 1960.

It was decided at the outset that both problems would be studied along the same lines. The glass strand should be obtained on forming tubes and untwisted to form a continuous strip of tape in which all the filaments are essentially parallel. For experimental coupling agents and sizes, the strand on the forming tubes could be obtained with a #630 starch-oil binder. The binder could be removed by heat and a solution of the new coupling agent or size applied.

We quickly found that the non-twisted strand could not be handled unless specially wound in a wide "X" lay with no strands parallel to allow the filaments to mesh. We also found that batch heat cleaning and dip finishing the strands while on the spools caused sufficient motion in the strands to intermesh the filaments of one strand with another and cause the strand to fray out on unwinding.

Equipment

To solve this problem of heat cleaning and finishing, we were forced to attempt continuous heat cleaning of the strand and immediately refinishing or resizing the strand. Over a period of time, the heat cleaning and finishing line evolved to the diagram given in *Figure 1*. It is important to note that the 2" diameter glass tube under the calrod heater is under a slight negative pressure at the entrance to the draft box on the glass strand discharge side. When oxygen is used, it is admitted at the other end of the tube with the entering five strands. It is believed that sufficient oxygen is added to significantly change the percentage of oxygen in the air used for heat cleaning, although the exact amount is not known at the time of writing. The strand is heated for

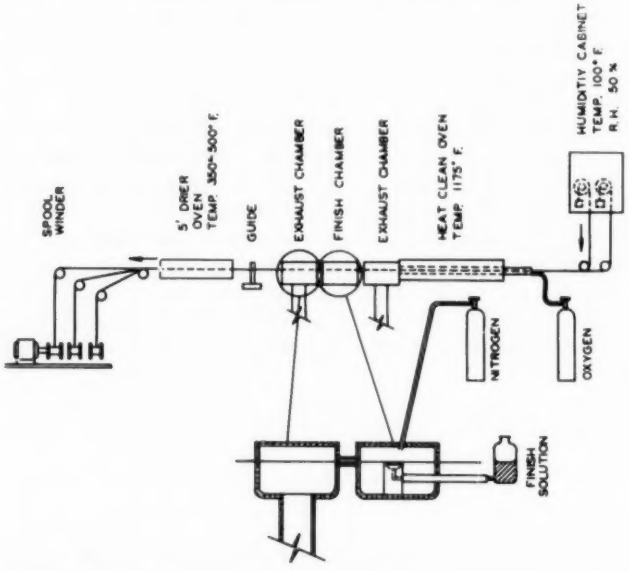


Figure 1. Heat cleaning and finishing line

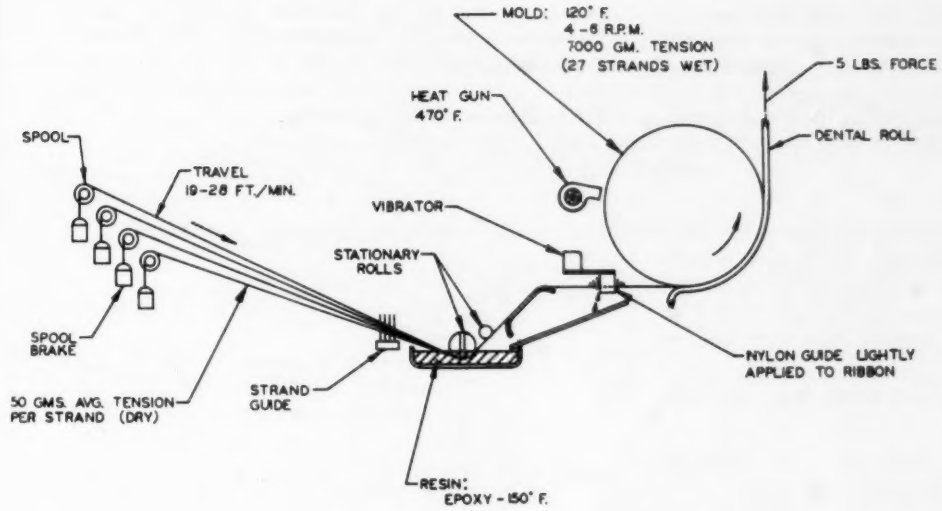


Figure 2. Hoop winding machine

from 8-12 seconds at 1175° ± 25°F to heat clean. With oxygen added to the air, the percentage residual size left on the strand is about 0.03% by weight glass. Heat cleaning in a like manner in air leaves a residual of 0.09%. It is likely that 0.03% of the residual in both cases is the water on the glass that is removed in heating from 160°F to the ignition temperature, 1100°F. Credence to this assumption was given by an attempt to measure the remains of the emulsifiers in the starch-oil size by nitrogen analysis to give essentially a 0.00% binder solids remaining on the oxygen-enriched air heat cleaned strand.

An advantage of continuous heat cleaning is that the strand may be heat cleaned and recoated without rubbing over itself or another solid surface. As shown in *Figure 1*, the glass strand following heat cleaning immediately enters a draft box that is connected to the size or finish applicator chamber. To obtain smooth, uniform application, spraying and pad application has been tried. Superior results are obtained with a soft cotton-batten-pad applicator from beneath and flooded from an outside reservoir that allows the coating solution to flow in as the five strands pick up the solution. The strand emerges from the size applicator box to pass through another draft box and thence to an oven, where the strands are dried at a temperature of 350-500°F for six to eight seconds.

With the draft box control, the size applicator box can be isolated from room air under a dry nitrogen blanket and anhydrous coupling agents such as NOL-24 or vinyl trichlorosilane applied from dry organic solutions. Also, an anhydrous coupling agent such as A-1100* (gamma amino propyltriethoxysilane) that is both water or toluene miscible may be applied from an anhydrous nonpolar solvent in a moisture-free atmosphere to the glass surface essentially free from unbound moisture. After drying and curing the coupling agent or size on the glass, the strand is wound on a spool for transfer to the hoop winding machine.

The hoop winding machine is shown in a diagram as *Figure 2*. Approximately twenty-five spools, one inch in diameter by one inch wide at the hub, are placed in a creel. Each end is brought to the resin impregnation tank directly and without touching any surface other than a guide. Each end is dynamically checked for equal tension. An adjustment at fifty grams is made with a prony brake. The non-twisted, ¼" wide ribbon of tapes from the twenty-five spools are run through the resin impregnation bath, over a curved spreader de-resining plate, and under a one-half-inch-wide curved, vibrating nylon guide just before entering the mold. The cylindrical mold is 18" in diameter and makes a ribbon-wound hoop approximately 1/4" wide by 3/16" thick. The mold is maintained at about 170-180°F by means of a circulating hot air gun with a one-inch diameter nozzle operating at 400°F. Excess resin is removed and the lay pressed together by a weighted, ½" diameter sewed roll of fabric, known as a "Dental Roll" at the dental supply houses. The hoops are cured on the molds in a circulating air oven for 16 hours at 250°F, followed by 4 hours at 360°F.

Testing

The 18" diameter hoops made as indicated above were machined to 0.1245 ± 0.015" thickness and 0.225 ± 0.04" width. The hoops were then divided around the diameter to 4" lengths and numbered consecutively from 1 to 13. They were then separated into three groups of four pieces per group and tested as follows: Pieces No. 1, 4, 7 and 10 were tested dry in flexure to flatten (designated convex); pieces 2, 5, 8 and 11 were tested dry in flexure to further curve (designated concave); and the third set—3, 6, 9, and 12 were tested wet (after 12 hours boil) in convex flexure. Both strength and modulus were determined. The 13th piece was retained. The glass content was found by igniting one-inch specimens cut from samples 1, 4, 7 and 10 after flexure testing. Four-point loading, as indicated in *Figure 3*, was used on all specimens and the loading rate was 0.05 inches per minute.

Weight gain and loss data was also determined. The samples were weighed before and after 12 hours of boiling. After testing, the wet samples were placed in an oven at 120°F for six days and weighed upon removal

* Trademark, Silicones Division, Union Carbide Corp., Tonawanda, N. Y.

from the oven. Castings having the same area per unit volume as the hoop specimens were made of the laminating resin. These samples were also weighed, boiled for 12 hours, weighed, dried for six days at 120°F, and weighed again. Thus the water gain and loss of the laminating resin was determined.

Calculations

The values of each four-inch-long piece was calculated as if each piece were straight. A 16 to 1 span to depth ratio was used with the two center span loading bars one-half inch apart on centers. For pieces 0.125" thick, the span between the bottom bars was 2.5" on centers.

The formulas derived for flexural strength and modulus were obtained from Roark *.

For determining flexural strength under ultimate maximum load, the following formula was used:

$$\text{Flexural Strength} = \frac{3P\,(L-d)}{2\,bh^2} = \frac{3P}{bh^2} \text{ for these pieces}$$

where: P = breaking load in pounds.
L = the thickness of the piece (about 0.25"). (2-½").
d = the distance between the upper bars (½").
b = the width of the piece (0.225").
h = the thickness of the piece (about 0.125").

An Instron Testing Machine was used. Failure was recorded on the chart with the left margin at 200 lbs. and at 100 or 200 lbs. full scale reading. All failures at ultimate load started as a shear failure adjacent to the glass filament or strand at from 92 to 100% of ultimate load. On the average, the first indication of failure occurred at 98% of ultimate load. Whether the ultimate failure was in tension, compression or shearing in the neutral plane, the first visible sign of flaw appeared around a filament, not through it.

The deflection curve, P/y, was measured over the initial fifty pounds loading with a one hundred pounds full scale range on the chart. The chart was driven by the motion of a Baldwin deflectometer arm set at the center of the piece. The rate of deflection was 0.05 inches per minute. Superimposing the effects of two symmetrical off-center loads on the center span deflection of a beam in flexure* and substituting values as for flexural strength, we find that:

$$E = \frac{P}{y}\,\frac{(L-d)}{4\,bh^3}\left[L^2 + Ld - \frac{d^2}{2}\right] = \frac{3.69}{bh^3}\cdot(P/y)$$

for these pieces.

where: E = flexural modulus in psi.
P = total load in pounds at the deflection reading.
y = deflection in inches at the center of the piece for any given load.
L = distance between lower bars (2-½").
d = distance between upper bars (½").
b = the width of the piece (0.225").
h = the thickness of the piece (about 0.125").

A straight line was drawn parallel to the curve for most data from 10 to 50 lbs. Under 10 lbs. there was excessive deflection. X-Y deflectometer action was discontinued over 50 lbs.

The coupling agent, binder or size on the strand was calculated from weighings made before and after a one-hour ignition at 1100°F. Samples were pre-dried before weighing by heating at 160°F for 14 hours. The quantity of coupling agent or size actually present on the strand is calculated in part from the size ignition loss minus the residual left from the heat cleaning. This adjusted ignition loss is corrected again to include that portion (ie, Si—O—) of the formulation that would not be removed at the ignition temperature. Obviously, this method, although it is easily and relatively quickly performed, has several sources of deviation. The amount of residual left on the strand can affect the low binder content (0.04-0.10%) values drastically. Some methods of application, at the bushing, for example, give great variations (1/3 fold) in a single set of six samples. However, in practically all of the cases reported below, the variation is not over two fold for six samples.

Wet pick up of the strand is calculated from the binder loading of the strand by converting the binder to a weight of unreacted solids and determining how much solution was needed to carry these solids at the concentration used. It is reported as percent solution picked up by the strand.

The variation of glass content from outside to inside of hoop was determined by slitting the one-inch test piece in half. It is reported as an average and high-low difference. Differences greater than 1.0% generally cause low dry or wet flexural strength (or both).

A quick method was used to determine the gain or loss of materials at the interface area during boiling to see if such a value could be related to the physical resistance of the piece. For the purposes of this article, the interface area is considered to be between the glass filament and the laminating resin. The interior of the glass is considered non-wetted by the water and any extractable material comes from the alkaline oxides on the surface, residual ignitable material left by heat cleaning or soluble portions of the coupling agents, resins or binder components in the size. It appears that the size

* Roark, Raymond J., "Formulae for Stress and Strain", Page 100, Case 12, Second edition 1943.

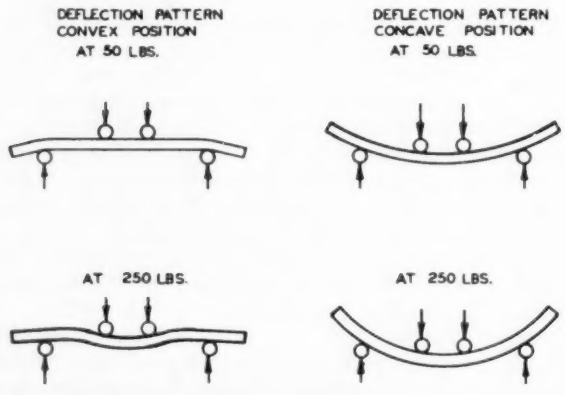


Figure 3. Application of four point load in flexure

Table 1. Sample of Data

Resin-Bonded Continuous Hoop Study Glass Content, Dry and 12-Hour Boil Flexural Strength, Solids Loss, and Water Gain at Interface 150 1/0 E Glass

The Effect of Adding Oxygen in Continuous Heat Cleaning

Hoop No.	Glass Content, % In-Out Difference	Glass Content, % Average	Flexural Strength × 10^3 psi Dry	Flexural Strength × 10^3 psi 12 hr Boil	Flexural Modulus × 10^6 psi Dry	Flexural Modulus × 10^6 psi 12 hr Boil	During 12 hr boil; at Interface Solids Loss %	During 12 hr boil; at Interface Water Gain, %
A. A-1100, 1% Solids, Water								
1. Continuous Heat-Cleaned in Air								
168	0.7	82.8	214.0	196.5	7.66	7.68	0.14	0.14
170	1.2	83.9	205.2	195.9	7.28	7.80	0.17	0.13
Average		83.3	209.6	196.2	7.47	7.74	0.15	0.13
			(93.7% Strength Retention)					
Adjusted to		85.0	214.0		7.7			
2. Continuous Heat-Cleaned in Oxygen-Enriched Air								
241*	2.0	84.8	245.4	236.1	8.36	8.29	0.15	0.03
240*	1.3	84.8	248.1	218.8	8.50	8.70	0.13	0.07
233	0.9	85.3	251.6	236.0	8.44	8.43	0.13	0.04
232	0.9	84.5	246.8	227.5	8.36	8.45	0.15	0.01
231	0.6	85.1	252.3	226.7	8.66	8.77	0.17	0.02
242	0.5	84.8	245.9	226.7	8.65	8.49	0.14	0.04
Average		84.9	249.2	229.2	8.53	8.54	0.15	0.02
			(92.2% Strength Retention)					
3. Batch Heat-Cleaned in Air (650°F Top Temperature)								
271	0.8	80.9	198.3	196.4	7.68	7.79	0.12	0.05
272	0.9	81.0	200.8	196.8	7.76	7.71	0.14	0.07
Average		81.0	199.6	196.6	7.72	7.75	0.13	0.06
			(98.5% Strength Retention)					
Adjusted to		85.0	216.0		8.3			
4. Applied as a 10% Solids Solution at the Bushing								
139	—	83.5	203.8	195.5	7.43	7.68	0.17	0.43
			(96% Strength Retention)					
Adjusted to		85.0	208.0		7.6			

(Table 1. Continues on Next Page)

components dissolve to any degree only if the size is poor or has not been properly applied.

To determine the solids loss at the composite interface, the weight gain of the castings of laminating resin passing through the full boiling-drying cycle was first reduced to its proper proportion in the glass-resin composite hoop sample and then added to the weight loss of the composite that had passed through the full boiling-drying cycle. Castings of the laminating resin, for example, have gained 1.39% on boiling 12 hours and lost 0.82% on six days drying at 120°F, giving a net gain due to absorbed water of 0.57%. It is assumed that the laminating resin in the composite sample absorbs the same proportion of water under the same conditions. Hoop #232 samples lost 0.06% by weight in the full boiling-drying cycle; the resin content was 15.6%. The water gain of the laminating resin portion at the end of the full cycle was (0.57 × 0.156) 0.089%; therefore, the solids loss at the interface after the full cycle is: 0.089 plus 0.06 or 0.15% by weight.

Continuation of Table 1

B. Binder, 2% Solids, 1 Part A-1100, 3 Parts 2.0 mol. VCHDO Plus 1.0 mol. 1-PE								
1. Continuous Heat-Cleaned in Air								
210*	1.4	83.0	203.0	179.0	7.51	7.68	0.12	0.38
211	1.3	82.4	212.2	188.8	7.51	7.75	0.11	0.24
212	0.9	82.6	215.8	212.0	7.73	7.96	0.17	0.60
Average		82.5	214.0	200.4	7.62	7.85	0.14	0.42
				(93.6% Strength Retention)				
Adjusted to		85.0	224.0		8.0			
2. Continuous Heat-Cleaned in Oxygen-Enriched Air								
261*	2.0	84.8	244.0	218.0	8.51	8.73	0.47	0.63
262	0.6	84.8	256.3	218.3	8.59	8.47	0.49	0.67
263	1.6	85.4	244.9	217.4	8.54	8.18	0.09	0.06
Average		85.1	250.6	217.8	8.57	8.33	0.29	0.36
				(86.8% Strength Retention)				

* These hoops have not been included in the average because of high differential in glass content.

The water adsorption at the interface after 12 hours of boiling is found in a like manner. It is further postulated that the solids lost in the full cycle are actually lost during the boiling and that they are replaced with water on a weight-for-weight basis. To remove the effect of water gain in the resin, all calculations are equated at the end of the drying cycle. The total water gain at the resin-glass interface is the sum of the total hoop change in weight (boil to dry) plus the solids loss minus the water lost in the laminating resin during the drying cycle. Continuing our typical example: Hoop #232; to the hoop weight change — 0.035% (a loss)— is added the solids loss, 0.14, to give 0.105%. From this value is subtracted loss of water during drying in the resin (0.82 × 0.156) 0.127% to give —0.02%. This indicates that there was no water gain other than the gain expected in the laminating resin through molecular storage. Further, the water did not replace all the interface solids loss, although this loss was normal (0.14%). This result is typical of an A-1100 coupling agent applied from 1% solids in water solution to 150 1/0 glass strand continuously heat cleaned in oxygen-enriched air and laminated with epoxy resin.

Data Presentation

The presentation of data in this paper will be restricted to include only one laminating resin, the diglycidyl ether of bisphenol A (Epon* 828) and methyl Nadic** anhydride, 100/91 parts respectively, plus 0.3% N,N-dimethyl benzyl amine as catalyst cured always in the same manner, 16 hours at 250°F plus 4 hours at 360°F. The glass will be 150 1/0 —E-glass

* Trademark, Shell Chemical Co.
** Trademark, National Aniline Division, Allied Chemical Corp.

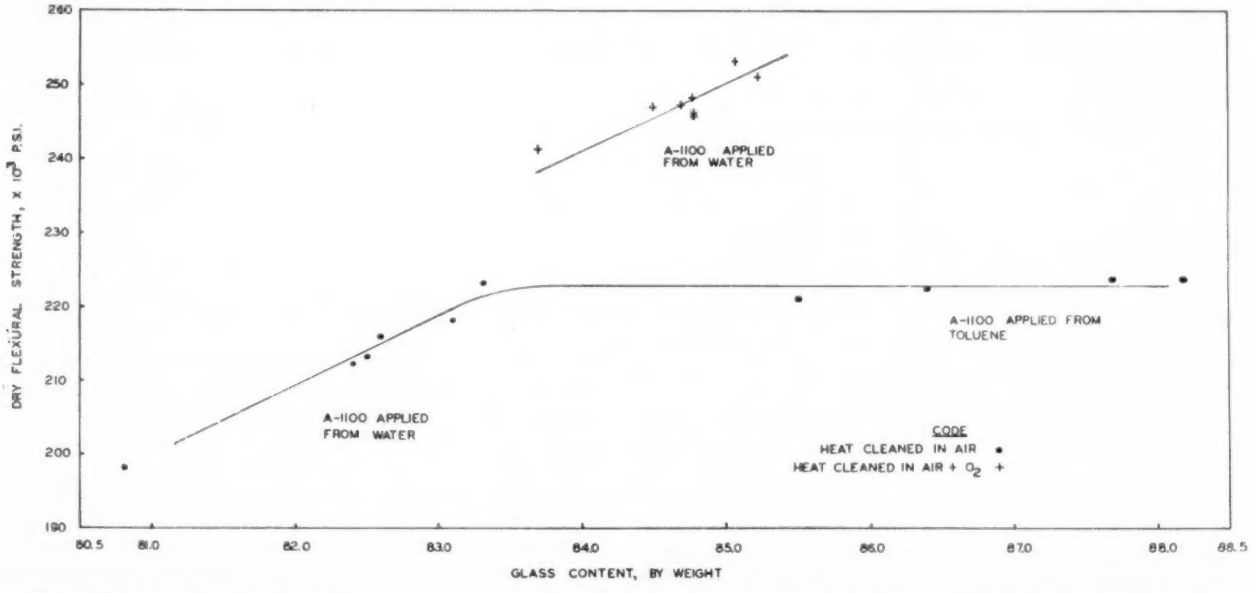


Figure 4. Flexural strength vs glass content for samples with A-1100, which were heat cleaned in air oxygen enriched air

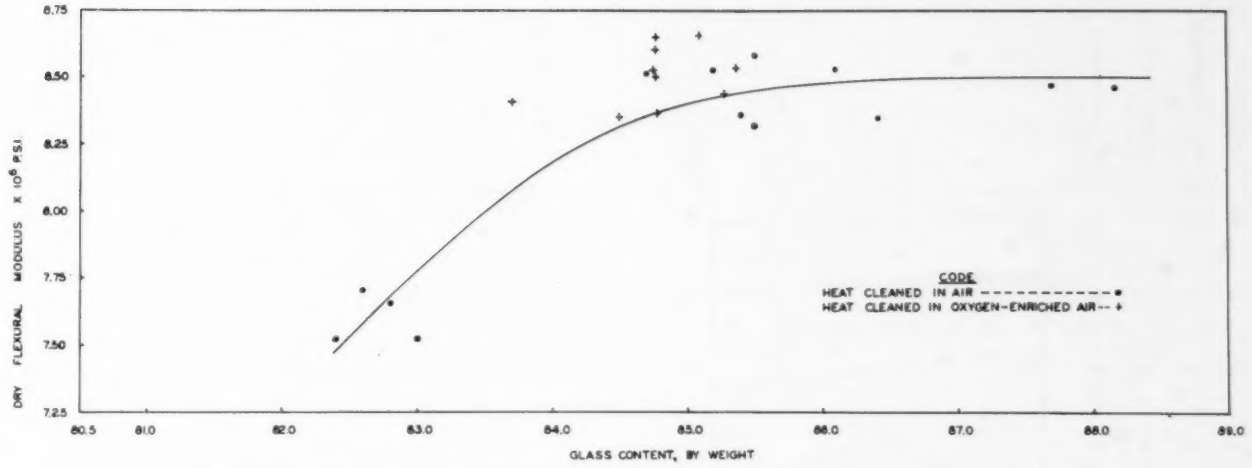


Figure 5. Flexural modulus vs glass content for samples heat cleaned in air or oxygen enriched air

having 204 filaments per strand. The presentation will be made in a series of comparative groups of data arranged to indicate the effect of a given change in formulation of the coupling agent size on the properties of the hoop made. All flexural strength and modulus properties are adjusted to 85% glass content in accordance with the curves given in *Figures 4 and 5*. In most cases, at least two hoop results are averaged for each value. Making this adjustment for glass content makes it possible to examine differences of over 2% in strength and 3% in modulus as significant.

The Condition of the Glass Surface

Coupling Agent A-1100: A-1100 (gamma amino propyl triethoxy silane) is applied from water solution to E-glass at the time of forming or after heat cleaning by batches on spools or heat cleaning. The strand is heat cleaned continuously, either in air or in oxygen, as shown in *Figure 6*. The abscissa from right to left is the percent residual starch-oil left on the strand after heat cleaning. Examination of the five parameters plotted brings forth the comment that:

1. The addition of oxygen during continuous heat cleaning gives a marked improvement over the other methods of preparation. Modulus is highest also, but the retention of dry flexural strength on boiling is slightly lower. Highest dry strength coincides with least water adsorption at the composite interface and highest wet pickup of size solution on strand.
2. In contrast, the application of a solution at high solute concentration at the bushing at extremely high speed is characterized by a low wet pickup. Possibly that is why there was the high adsorption of water on boiling. The solids appeared to form bridges more readily on this strand, showing poor coverage of the surface with moderately lower strength and modulus.
3. Heat cleaning in air, either batch (16 hours, 550°F + 48 hours, 650°F) or continuous, gave equivalent results except in dry modulus. Practically, however, the batch heat cleaned spools could only be unwound if strands were first twisted one turn per inch before winding.

Coupling Agent Z-6020: Applying Z-6020* [H_2NR-$NHR'Si$-$(OCH_3)_3$ from water solution to E-glass at the time of forming and after continuous heat cleaning the strand in oxygen-enriched air is shown in *Figure 7*. In contrast to the improvement shown in continuous heat

* Trademark, Dow Corning Corp., Midland, Mich.

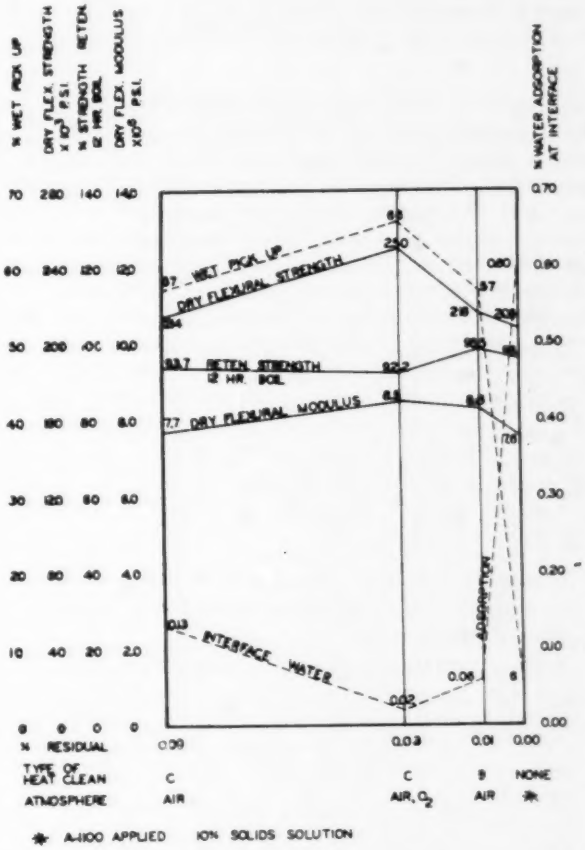


Figure 6. Hoop physical properties and the condition of the glass surface, using coupling agent A-1100 1% in water. Results are adjusted to 85% glass by weight.

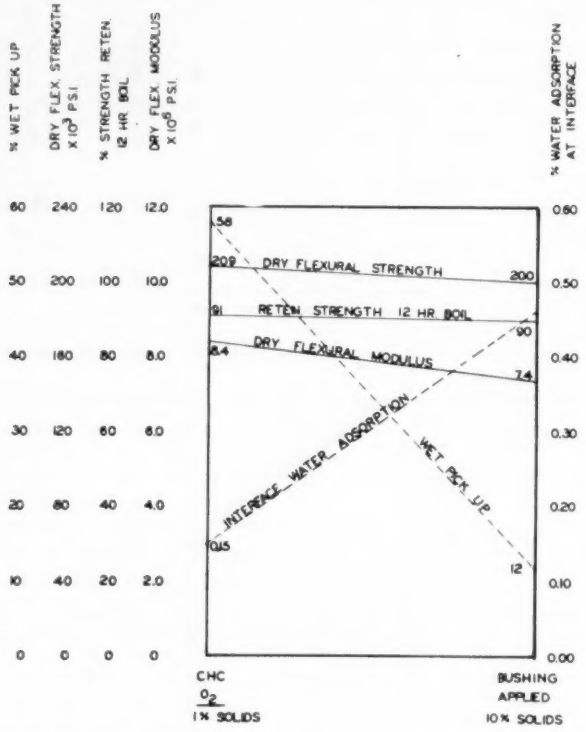


Figure 7. Hoop physical properties and the condition of the glass surface using coupling agent Z-6020 in water.

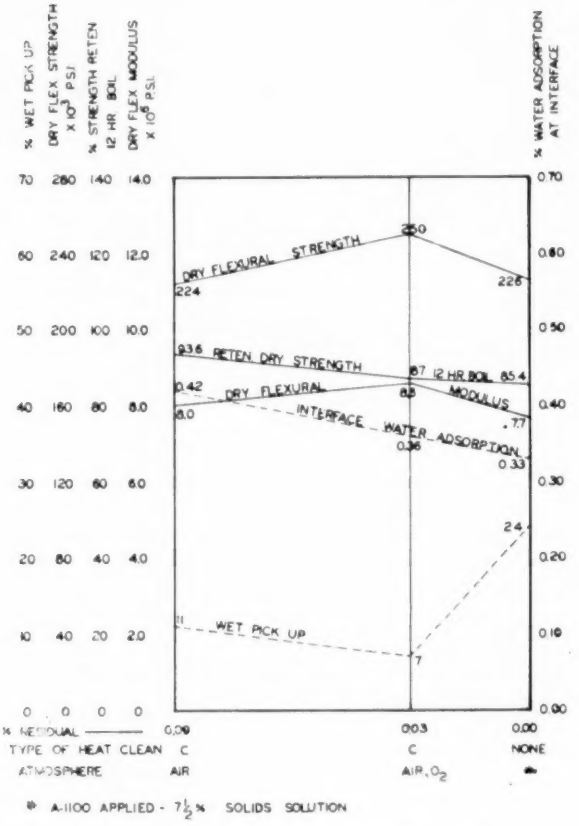

% WET PICK UP
DRY FLEX. STRENGTH X 10³ P.S.I.
% STRENGTH RETEN. 12 HR. BOIL
DRY FLEX. MODULUS X 10⁶ P.S.I.
% WATER ADSORPTION AT INTERFACE
DRY FLEXURAL STRENGTH
RETEN. DRY STRENGTH
DRY FLEXURAL MODULUS
INTERFACE WATER ADSORPTION
WET PICK UP
% RESIDUAL TYPE OF HEAT CLEAN ATMOSPHERE
AIR
AIR, O2
NONE
* A-1100 APPLIED - 7½% SOLIDS SOLUTION

Figure 8. Hoop physical properties and the condition of the glass surface using 1 part A-1100, 3 parts 2 mol vinyl cyclohexene dioxide plus 1 mol 1-piperazine ethanol 2% in water.

cleaning in oxygen-enriched air and coating with A-1100, the like product coated with Z-6020 is but slightly improved except in modulus. Since the Z-6020 appeared to bulk or bridge more on the strand that A-1100 at the same wet pickup rate, the poorer properties under optimum conditions may be attributed to a lower area coverage of the strand for bonding (higher interface water adsorption). In all cases the pickup of the Z-6020 solution was more irregular than the A-1100.

Size Formulation—1 part A-1100, 3 parts 2.0 mol VCHDO (vinyl cyclohexene dioxide) + 1.0 mol 1-PE (1-piperazine ethanol): Applying the above binder designated as D&R F-1 size under the same series of conditions, except batch heat cleaning as the A-1100 but applying from 2% solids solution in water brought the results shown graphically in *Figure 8*, compared with *Figure 6* below:

1. The continuous heat cleaning in oxygen-enriched air as with A-1100 alone gave results superior to the other methods tried.
2. With all methods of strand preparation, the D&R F-1 size gave superior handling properties to the strand as compared to A-1100 alone. However, applied at the bushing the strand handling properties were markedly superior over A-1100 alone.
3. The comparatively parallel lines for wet pick up and interface water adsorption indicate the evenness with which the binder solution wets the strand under a variety of conditions. Again, it appears evident that the oxygen added during heat cleaning actually improves the bonding of the coupling agent to the glass substrate to possibly allow the creation of more bonds, some of which are possibly not ionic but of the hydrogen type and more susceptible to water attack. Possibly the oxygen is adsorbed on the surface to increase the number of available sites.

Solvent Wetting of an E-Glass Surface as a Function of its Polar Nature

Coupling Agent A-1100: The application of A-1100 in different solvents to the surface of E-glass strand heat cleaned in air had some very interesting results, as shown in *Figure 9*. As indicated above, the amino silanes applied from water solution tend to bridge the filaments and hold them in alignment. From organic solvents, ethanol, dioxane and toluene, A-1100 was applied under anhydrous conditions. The toluene was purchased dry and sulfur-free. The dioxane was used as received and may have contained a very small quantity of water. It is suggested that the application of A-1100 from dry toluene under anhydrous conditions to a glass strand continuous heat cleaned and transported to the finish box without adsorption of unbound water is through a reaction of the ethoxy groups directly with the silanols or bound water within 400 Angstroms or less of the glass surface. The reaction would produce ethanol but no silanol groups. The coupling agent could chain extend

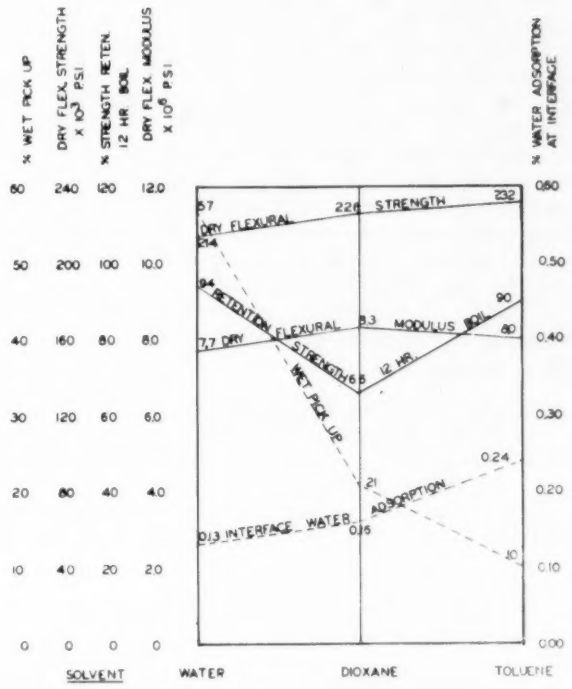


Figure 9. Hoop physical properties and solvent wetting of an "E" glass surface as a function of its polar nature. Strand was heat cleaned in air and a 1% A-1100 solution applied.

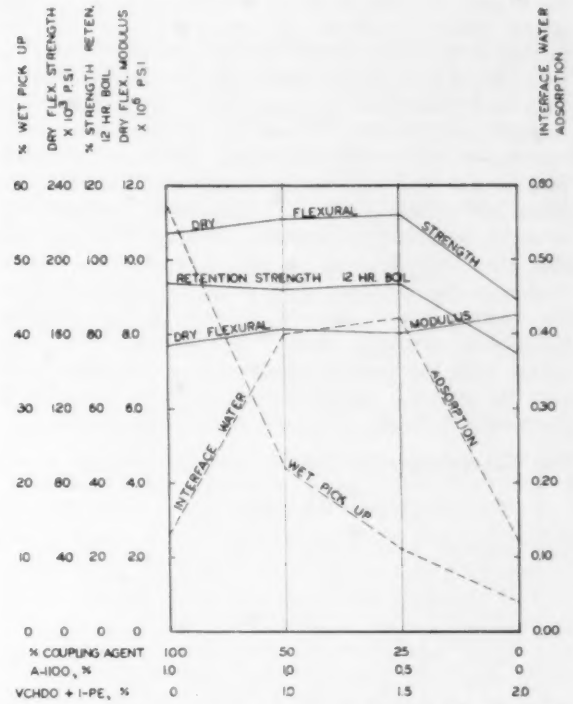


Figure 10. Size formulation (coupling agent, A-1100, VCHDO 1-PE and water). Effect of varying resinous ingredients and coupling agents on hoop physical properties. Filaments are continuously heat cleaned in air as in Figure 1.

only by the reaction of two ethoxy groups to form a crosslink with diethyl ether as a reaction product, a slow reaction at best. Hoops made from A-1100-toluene solution of any concentration from 0.1 to 4% do not bridge the filaments and do not protect the strand well. From 0.1 to 1.0% concentration toluene solutions, the hoops have about the same glass content, 87-88% by weight, and about the same physical properties. In contrast, it is difficult to make a hoop from glass coated with 1% A-1100 water solution as high at 86% glass and it takes extreme care to do it. By holding the filaments in position relative to each other in the strand, excessive movement and internal abrasion is reduced. By reducing the quantity of A-1100 applied from 1.0 to 0.1%, a hoop of higher glass content (86%) will be made and physical properties will improve for this reason. However, at these low application contents, the strand is more difficult to handle due to a lack of bridging. As compared to A-1100 applied from toluene, A-1100 applied from water hydrolyzed in solution to the silanol. These silanols react to form soluble linear, and possibly crosslinked, polymers. It is possible the residual alkali metal ions held on the surface of the E-glass by bonding to the amphoteric metal oxides such as Al_2O_3 and MgO promote this polymerizing reaction and aid in the bridging effect. Unless there is a definite state of unbalance in the silane structure, the solids loss at the interface runs 0.13-0.16% in water applications of alkyl alkoxy silanes to E-glass and laminated with epoxy resins. If application is from toluene the solids loss jumps to 0.28%.

Changing the Relative Quantities of Coupling Agent and Resin Components in a Size Solution

Size Formulation: A-1100 (2 mol VCHDO, 1 mol 1-PE)-water.

1. Continuously heat cleaning in air. In *Figure 10* there is presented a plot to show the replacing of the resinous ingredients with coupling agent to find the effect on hoop physical properties. The resinous combination of 2.0 mol vinyl cyclohexene dioxide and 1.0 mol 1-piperazine ethanol was designed to allow the linear epoxides to react with the secondary amines of the piperazine and the primary amine of the amino alkyl alkoxy silane (coupling agent) and leave the ring epoxides free to react with the anhydride in the laminating resin. This appeared to be the manner in which the reaction proceeded. The VCHDO + 1-PE alone tended to increase the modulus of the size coating, while the A-1100 alone had an opposite effect. The comparatively high strength retention may be attributed to the higher precentage retained solids on the surface of the glass (0.09% by weight glass) expected from continuous heat cleaning in air. Comparatively low dry flexural strength was obtained along with excellent water resistance properties of the coating as seen by a low water adsorption. The wet pick up of the size is a function of the quantity of coupling agent in solution; it is also affected by the relative quantities of dissolved organic materials.
2. Continuously heat cleaning in oxygen-enriched air.

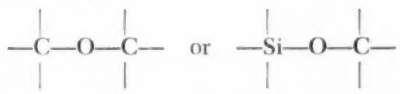
In *Figure 11*, the ratio of coupling agent to total solute definitely affects the magnitude of the wet pickup of the size solution on the strand. Continuous heat cleaning in oxygen-enriched air reduces the residual starch-oil solids to about 0.03% by weight glass. A high consistent dry flexural strength and modulus is maintained under all conditions, although the thickness of the size application varies six fold. The absence of coupling agent considerably reduces the strength retention properties on boiling. It is probable that the 34% flexural strength retention on boiling is due to the comparatively excellent resistance that the coating has to rupture as seen by the comparatively low interface water adsorption. When compared with the case of binder-only in air, the retention of strength properties on boiling is inversely proportional to the interface water adsorption.

Size Formulation—A-1100 (2 mol 1,4-DGOB, 1 mol 1-PE)-water.

1. Continuously heat cleaned in oxygen-enriched air. In *Figure 12* a plot of variables is given to show the effect of changing the water-soluble diepoxide to 1,4-diglycidoxy butane (1,4DGOB). This diepoxide has two linear epoxides with the same Lewis base activity that are glycidoxy in nature like diglycidyl ether of bisphenol A (Epon 828). Its effect on the hoop properties are to make the size coating even more flexible than with A-1100 alone, to the point of affecting the dry strength as well as modulus. The epoxy resin without coupling agent is very susceptible to water attack, giving high interface water adsorption. As with the other cases, the wet pickup is a direct function of the ratio of coupling agent present in the size. Hoop flexural strength retention is maintained amazingly well at low dilutions of coupling agent until the coupling agent is omitted. This shows the preferential attraction of the alkyl silanol for the glass surface.

Changing the Groups on Amino Alkyl Alkoxy Silane

A. Continuously heat cleaning in oxygen-enriched air.
   1. Using A-1100 as the standard on *Figure 13*, the following deductions may be made:
      a. The wet pickup of the solution on the strand is greatly increased by additional oxy groups, whether they be



and decreased somewhat by amine groups. The Z-6020 shows up particularly poorly in

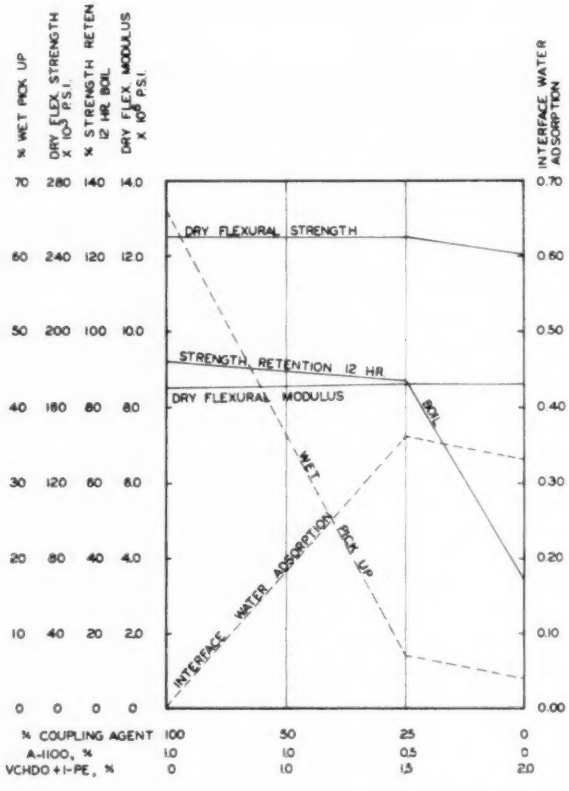


Figure 11. Size formulation (coupling agent, A-1100, VCHDO, 1-PE and water). Effect of varying resinous ingredients and coupling agents on physical properties. Filaments are continuously heat cleaned in oxygen enriched air.

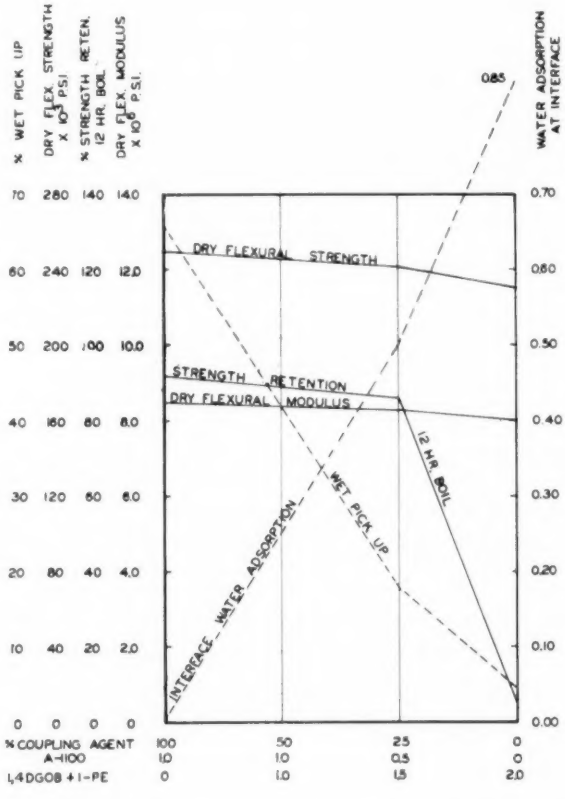


Figure 12. Size formulation (coupling agent A-1100; 1,4 DGOB 1-PE and water). Effect of varying resinous ingredients and coupling agents on physical properties. Filaments are continuously heat cleaned in oxygen enriched air as in Figure 2.

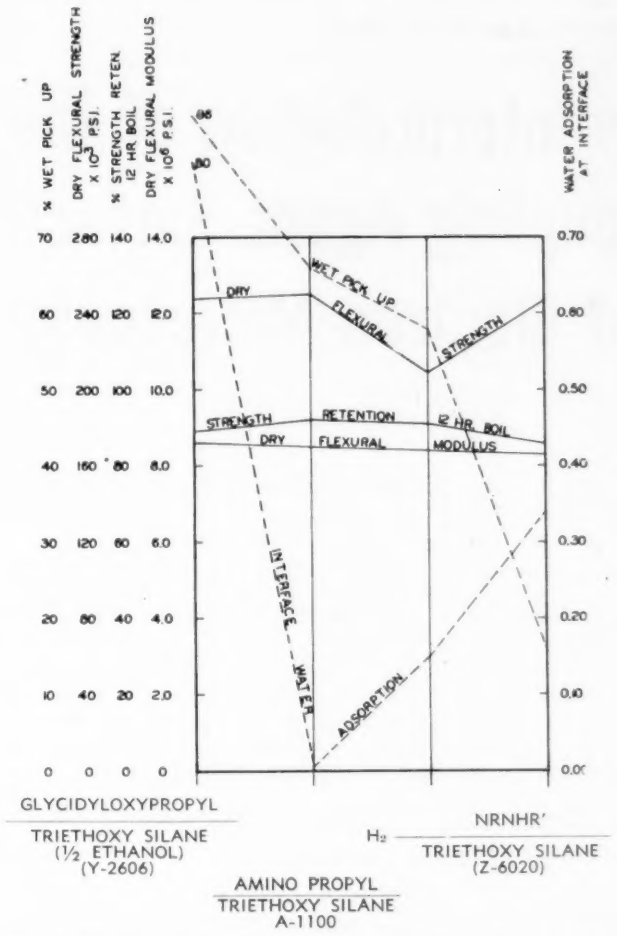

% WET PICK UP
DRY FLEXURAL STRENGTH X 10³ P.S.I.
% STRENGTH RETEN. 12 HR. BOIL
DRY FLEXURAL MODULUS X 10⁶ P.S.I.
WATER ADSORPTION AT INTERFACE
70 280 140 14.0 0.70
60 240 120 12.0 0.60
50 200 100 10.0 0.50
40 160 80 8.0 0.40
30 120 60 6.0 0.30
20 80 40 4.0 0.20
10 40 20 2.0 0.10
0 0 0 0 0.00
WET PICK UP
DRY FLEXURAL STRENGTH
STRENGTH RETENTION 12 HR. BOIL
DRY FLEXURAL MODULUS
INTERFACE WATER
ADSORPTION
GLYCIDYLOXYPROPYL TRIETHOXY SILANE (½ ETHANOL) (Y-2606)
AMINO PROPYL TRIETHOXY SILANE A-1100
H₂ NRNHR' TRIETHOXY SILANE (Z-6020)

Figure 13. The effect on physical properties by changing the groups on amino alkoxy silane water solution of 1% solids. Filaments are continuously heat cleaned in oxygen enriched air as in Figure 1.

dry flexural strength due, as mentioned above, to the tendency it has to bulk and bridge excessively on the filaments. Comparison with A-1100 shows an indication of this effect through increased water adsorption of Z-6020 hoops. Y-1902, the delta amino butylmethyl diethoxy silane, shows amazing coverage and strength retention for the low wet pickup of 16% solution on the strand. The methyl substitution for an ethoxy group on the silane would make it a more open filter for leaching (water-permeable) than A-1100. The increased interface water adsorption is due to a greater interface solids loss that, in turn, may be attributed to a water permeability of the coupling agent coating. The high interface water gain of the Y-2606 must be attributed to another mechanism because the water gain greatly exceeds the solids loss at the interface. It may be due to the four-fold increased wet pickup and the ether linkage of the increased length of the carbon chain (the glycidoxy propyl unit) to store water.

Summary

In 18-inch-diameter continuous filament wound hoops at 85% glass, alkoxy silane type coupling agents were examined as a component of a size applied to continuous glass filament strand. The values of the bushing application, batch heat cleaning, and, for the most part, continuous heat cleaning in air and in oxygen-enriched air followed by application from water and organic solvents have been determined.

In general, it has been shown that the highest flexural properties are found and maintained by applying the coupling agents or size containing the coupling agent in water to glass strand continuously heat cleaned in oxygen-enriched air. The amount of solution picked up or wetted to the strand is related to ratio of coupling agent to organic compounds present in the size solution. The wetting ratio, in extreme, can be in the order of fifteen to one, while coupling agent to organic compounds in relative proportions vary from 100% to 0%, respectively. The choice of groups in the coupling agent also affects the degree to which a solution of the coupling agent in water wets an E-glass surface. The effect of different solvents is illustrated to show that there is to be expected under anhydrous conditions a different reaction with the glass than when water is used as the solvent.

In general, it may be stated that the dry flexural strength is affected by only major changes in the character and deposition of the size coating on the glass, although the initial fractures are initiated in or near the size coating. However, the dry flexural strength is affected by the quantity and character of residues left by heat cleaning on the glass surface and by the handling of the strand during processing.

Retention of dry flexural strength properties is related primarily to the presence or absence of a coupling agent on the glass surface. A major factor for poor retention otherwise is an extremely irregular application technique or the retention of abnormally high residual solids content in heat cleaning the strand to remove a starch-oil finish.

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Dixon Wetherbe—Design and operation of the hoop winding equipment.

Arthur Karszes and Robert I. Lent—Testing.

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The Fiberglas and Glass Research Divisions of Pittsburgh Plate Glass Company have contributed the glass strand used, and the Silicones Division of Union Carbide Corporation contributed the experimental finishes.

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A New Interpretation of the Glass-Coupling Agent Surface Through Use of Electron Microscopy

S. Sterman and H. B. Bradley

Union Carbide Corp., Silicones Division and Linde Co., Tonawanda, N. Y.

- *Each coupling agent has groups reactive with the glass surface and organic resin*
- *Higher than calculated monomolecular loadings are required because of capillary buildup*
- *High degree of agglomeration suggests techniques for applying monomers directly to clean glass*
- *Electron microscopy is a useful tool for studies of finishes*

There has been much speculation over the years as to whether the coupling agents, vinylsilane (Union Carbide A-172), *gamma*-aminopropyltriethoxysilane (Union Carbide A-1100) and methacrylato-chromium complex (DuPont Volan A), exert their effect through physical or chemical interaction with the two surfaces involved.

It is the purpose of this paper to show that (1) the glass-coupling agent interaction is important and that both physical and chemical effects are involved, (2) that the coupling agent-resin interaction is important and chemical in nature, (3) that higher than calculated monolayer loadings of coupling agents are needed because of poor distribution of the coupling agents on the surface with concentration in the interfilament capillaries of the glass strand, and (4) agglomeration of the coupling agent on the glass surface occurs because of deposition from aqueous solution which causes hydrolysis and condensation to low molecular weight polymers before actual contact with the glass. Uses and properties of coupling agents as sizes and finishes are referred to in the attached bibliography.

General Chemistry of the Coupling Agents

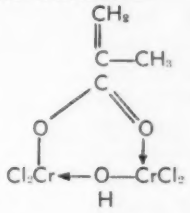
Table 1 shows the most widely used coupling agents. Some of these are used in more than one commercial process and may have several designations. A great many other coupling agents have also been made and used with good results, but have not reached commercially significant use.

The significant point common to these coupling agents is that each has a group reactive with the glass surface, and each has a group reactive with the organic resin; factors shown in more detail in the tables. *Table 2* shows schematically and in simplified form the hydrolysis of the silanes to the silanol form. The silanol then is capable of condensing not only with itself but also with the silanol groups of the glass surface. *Table 3* demonstrates the same essential reactions for the methacrylate-chromium compounds.

Table 4 shows schematically the reaction of the glass bonded vinyl silyl group with typical components of unsaturated polyester resins. While it is very difficult to show rigorously on the interface in a completed laminate structure that the vinyl silyl group chemically reacts with maleate or styrene unsaturation, these reactions have been demonstrated in bulk, solvent and emulsion copolymerization work. While the reactivity ratios show that vinylsiloxane-organic unsaturated compound copolymerization is less favorable than organic homopolymerization, nevertheless clearly sufficient vinylsiloxane is copolymerized to accomplish the bonding postulated.

Table 5 similarly shows the reaction of *gamma*-aminopropyltriethoxysilane with epoxy, methylol-phenol and methylol-melamine classes of resins. These reactions are readily observed in bulk. If equivalent amounts of aminoalkylsilane and, for example, epoxy resin are mixed, they react vigorously with a typical exotherm and gelation. When this silane compound is used, it is

Table 1. Commonly used Coupling Agents for Glass

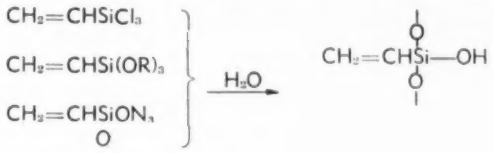
Chemical Product Code	Chemical Mfg. Co.	Chemical Structure	
A-150	Union Carbide	$CH_2=CHSiCl_3$	Vinyltrichlorosilane
A-151	Union Carbide	$CH_2=CHSi(OC_2H_5)_3$	Vinyltriethoxysilane
SS-2D-N	Cowles	$CH_2=CHSiON_3$ (O)	Sodium Vinyl Silanolate
A-172	Union Carbide	$CH_2=CHSi(OC_2H_4OCH_3)_3$	Vinyl Tris (2-Methoxyethoxy)silane
A-1100	Union Carbide	$NH_2(CH_2)_3Si(OC_2H_5)_3$	Gamma-Aminopropyltriethoxysilane
Volan	DuPont		Methacrylato Chromium Chloride

sometimes desirable to decrease the normally used amine catalyst to compensate for its activity. *Table 6* demonstrates rather convincingly in practical terms that the above postulated specific reactivities are significant.

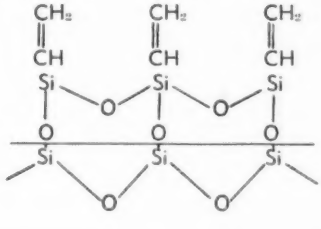
Under the polyester system described in *Figure 6*, note that vinyl tris[2-methoxyethoxy] silane is distinctly superior to that of a heat-cleaned cloth (finish 112). Much more important from the view of understanding mechanism and demonstrating chemical reactivity is the fact that vinyl tris[2-methoxyethoxy] silane is far superior to Union Carbide Y-1059 finish, which is exactly like the former except for the substitution of ethyl for the vinyl group. Both compounds give water repellency to the cloth; only the vinyl group gives wet strength. The ethyl compound is actually inferior to heat-cleaned (112) cloth.

Table 2. Reaction of Silanes with Glass

A. Controlled Hydrolysis and Partial Condensation:



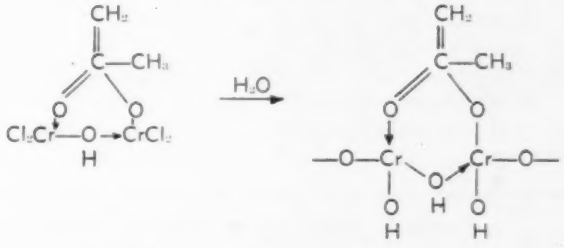
B. Reaction of Silanol With Surface Bonded OH of Glass:



For melamine, phenolic and epoxy resins, it is clear from *Table 6* that the vinylsilane is distinctly inferior to the *gamma*-aminopropyltriethoxysilane, as would be expected in terms of specific chemical reactivity. The 112 finish is very poor. The chrome finish in our tests, while quite good generally, is inferior in wet strength and especially in high-temperature-aged properties to the silane finishes. In the epoxy section, it should be noted that adhesion of epoxy to glass is sufficiently good so that aging tests must be run for longer times to demonstrate these differences.

Table 3. Reaction of Chromium Complexes with Glass

A. Controlled Hydrolysis and Partial Condensation:



B. Reaction with Surface Bonded OH of Glass:

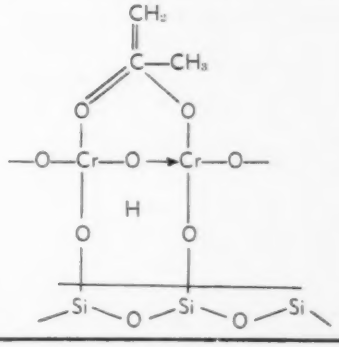
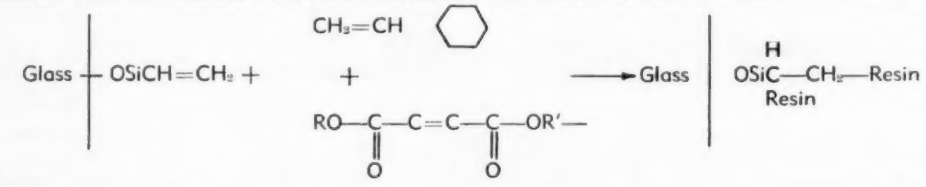


Table 4. Reaction of Vinylsilane with Polyester



Performance of Laminates as a Function of Coupling Agent Loading

If the "chemical bridge" mechanism of coupling agent action is true, then a monolayer on the glass should give optimum performance in laminates. However it was proven that more than a monolayer is actually needed.

Table 7 and *Figure 1 and 2* show flexural strength as a function of vinylsilane loading for a polyester-181 glass laminate. Note that wet strength retention is very low at one molecular layer (0.02-0.04% silane) and rises with silane loading to an optimum plateau at 0.25% silane or higher. This 0.25% loading corresponds to about eight molecular layers. In commercial practice, a somewhat higher loading is recommended to take care of normal production variations and to insure operation on the plateau of good performance. This performance plateau then remains constant until the loading rises to about 2% silane or about 70 molecular layers. Presumably the slight drop in strength is indicative of a weakening in bonding of the vinylsiloxane to itself at this level.

The calculation of weight of a molecular layer of vinylsiloxane (Union Carbide A-172) was as follows:

Surface area 181°-112 cloth	0.1-0.12 m^2/gram°°
Area covered by one molecule of vinylsiloxane, $CH_2=CHSiO_{3/2}$	13 Å°°°
Area covered by one gram, one molecule thick	280 m^2/gram
Weight per cent on 181-112 cloth for monolayer	0.02-0.04%

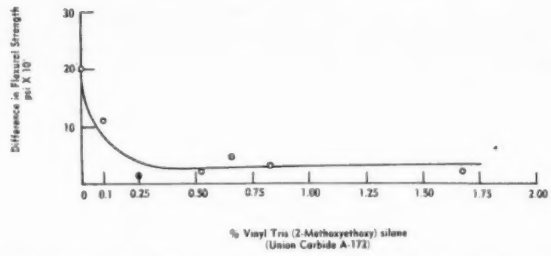

Difference in Flexural Strength psi X 10
30
20
10
0 0.1 0.25 0.50 0.75 1.00 1.25 1.50 1.75 2.00
% Vinyl Tris (2-Methoxyethoxy) silane (Union Carbide A-172)

Figure 1. Plot of Difference between dry flexural strength and flexural strength after two hour boil. 0.25% A-172 appears to be a minimum loading requirement.

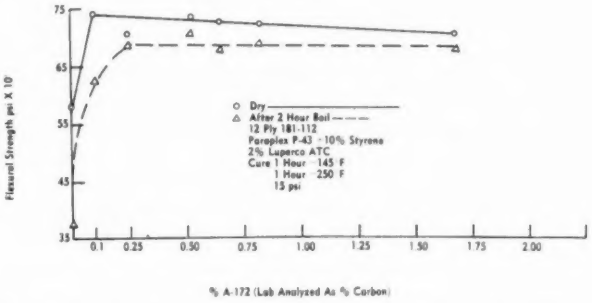


Figure 2. Vinyl tris (2-methoxyethoxy) silane (A-172) vs loading

° 181 is an Owens Fiberglas Corp. fabric weave.
°° BET nitrogen method and also by surface area calculation from dimensions of filaments.
°°° From Stuart and Briegleb scale molecular model (Lapine Company) 1 cm = 0.67 Å.

Table 5. Reaction of Gamma-Aminopropylsilane with Epoxy, Phenolic, Melamine Resins

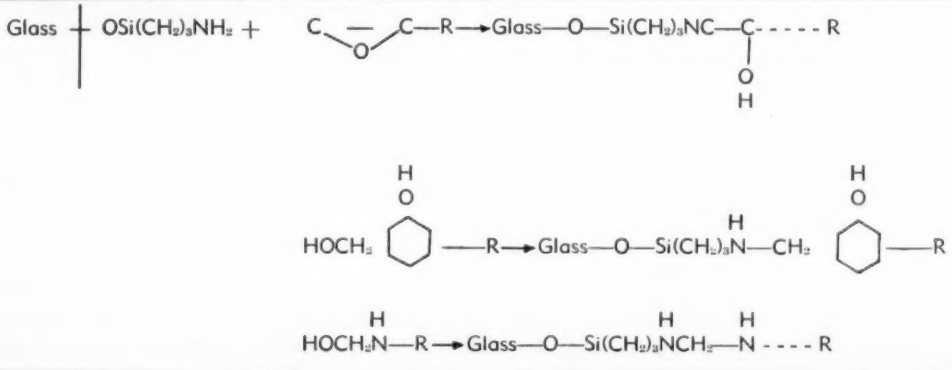


Table 6. Specificity of Coupling Agent—Resin System for Optimum Performance as Evidence of Chemical Interaction

Finish	Dry	After 2-Hour Boil	% Retention
Polyester[1]—Flexural Strength, psi			
A-172	72,000	68,000	94
Y-1059 (Ethylsilane)	43,500	30,000	69
A-1100	37,500	18,000	48
112	60,000	35,000	58
Chrome-Finish	72,000	62,000	86
Melamine[2]—Flexural Strength, psi			
A-172	31,500	28,000	89
A-1100	90,000	85,000	94
112	38,000	27,000	71
Chrome-Finish	68,000	65,000	95
Phenolic[3]—Flexural Strength, psi			
	Dry	**After 100-Hours at 500°F.**	**% Retention**
A-172	60,000	18,000	30
A-1100	80,000	55,000	70
112	69,000	14,000	20
Chrome-Finish	82,000	33,000	40

	Dry	After 2-Hour Boil	% Retention	72-Hour Boil	% Retention
Epoxy[4]—Flexural Strength, psi					
A-172	80,600	84,400	105	38,000	47
A-1100	81,000	75,000	93	55,000	68
112	73,600	53,500	75	—	—
Chrome-Finish	83,500	—	—	59,000	71

[1] **Polyester Laminate Description:**
12 ply-181 cloth. 35% resin content. Wet layup using Paraplex P-43 (Rohm and Haas) diluted with 10% styrene, catalyzed with 2% Luperco ATC. Pressed to ⅛" stops for 1 hour at 145°F., followed by 1 hour at 250°F.

[2] **Melamine Laminate Description:**
181-112 cloth coated with 60 wt-% solution of Cymel 405 (American Cyanamid) in water containing 5 wt-% n-butanol. Cloth "B" staged 2½ minutes at 135°C. 12 ply prepreg placed in press preheated to 155°C. Pressed at 1000 psi for 15 minutes. 35% resin content.

[3] **Phenolic Laminate Description:**
181-112 cloth coated with Plaskon V-204 (Plastics and Coal Chemical Div., Allied Chemical). Cloth "B" staged 2-3 minutes at 135°C. 13 ply prepreg, 30% resin content, placed in preheated press. Contact pressure 6-8 minutes at 290°F. followed by 30 minutes at 290°F. and 200 psi. Postcure 24 hours each at 250°F., 300°F., 350°F. and 400°F. Specimens to be tested at 500°F., aged 100 hours at 500°F.

[4] **Epoxy Laminate Description:**
12 ply 181 cloth, 30% resin content. Wet layup using Epon 828 (Shell) catalyzed with 15 grams per 100 grams resin of metaphenylene diamine. Press cure—contact pressure 8-10 minutes at 250°F. followed by 22 minutes at 250°F. and 200 psi. ⅛" laminate postcured 1 hour at 200°C.

The 181 cloth used in these systems was commercially finished with recommended loadings. Y-1059 (ethylsilane) finish was laboratory applied to give loading equivalent to A-172.

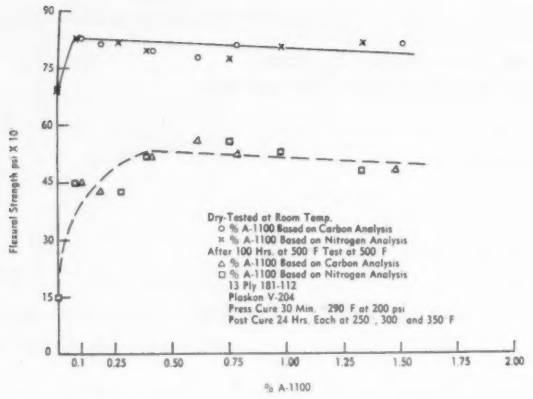

Flexural Strength psi X 10
% A-1100
Dry-Tested at Room Temp.
○ % A-1100 Based on Carbon Analysis
× % A-1100 Based on Nitrogen Analysis
After 100 Hrs. at 500 F Test at 500 F
△ % A-1100 Based on Carbon Analysis
□ % A-1100 Based on Nitrogen Analysis
13 Ply 181-112
Plaskon V-204
Press Cure 30 Min. 290 F at 200 psi
Post Cure 24 Hrs. Each at 250 , 300 and 350 F

Figure 3. Gamma-aminopropyltriethoxysilane (A-1100) performance vs loading. Optimum performance begins between 0.1 and 0.25% A-1100.

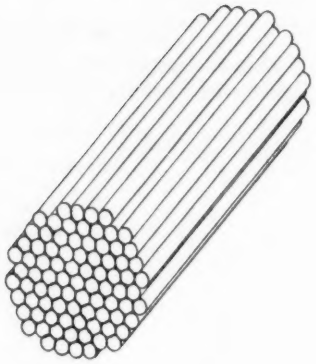


Figure 4. Lengthwise view of glass strand showing corrugated surface character.

Similar data for *gamma*-aminopropylsilane (Union Carbide A-1100) are presented in *Table 8* and *Figure 2* with 500°F. performance rather than wet strength as the criterion of performance. The data at 500°F. show a plateau of optimum performance beginning between 0.1 and 0.25%.

Similar data could not be obtained for Du Pont Volan A because the recommended procedure gave only about 0.15% loadings and higher loadings could not be obtained because the water wash removed the excess even if heat set first.

Degree of Bonding of Finish to 181 Cloth

In an attempt to explain the need for higher loadings, a series of extraction tests with water in a Soxhlet apparatus was then run on all three finishes to study degree of bonding. A vinylsiloxane (Union Carbide A-172) finished cloth showed essentially no loss of silane even after several days of extraction. An aminoalkylsilane (Union Carbide A-1100) finish showed removal of the outer layers but the adherence of a tightly-bonded polymer close to the glass. Depending on the loading, 75-94% of the original amount was removed, leaving in each case about 0.06% A-1100 on the cloth or about 2-3 molecular layers. This is shown in *Table 9*. 181 Volan A finished to about 0.5% Volan A loading extracted very readily to about 0.15% to 0.2% loading based on Cr and about 0.1% based on the methacrylate grouping but this remained constant on longer extraction. See *Table 10*.

It should be noted that vinylpolysiloxane polymer (A-172) is insoluble in water and that it is thus not surprising that none was removed from the glass by water extraction. However, it has been reported that toluene extraction tests on A-172-finished cloth remove the outer layers and leave a tighly-bonded layer, in a manner analogous to the aqueous extractions above for A-1100 and Volan A. Polymers of A-1100 and Volan A are, of course, water soluble.

Table 7. Relationship of Flexural Strength Properties of Polyester Laminates to A-172 Loadings on the Glass Cloth Reinforcement

% A-172 by Carbon Analysis	Average Flexural Strength, psi		Per Cent Retention	% Resin Content	Thickness (Inches)
	Dry	2-Hr. Boil			
—	58,200	37,300	64.2	34.7	0.116
0.10	74,200	62,500	84.3	34.0	0.116
0.25	70,400	69,200	98.3	34.6	0.117
0.52	73,800	70,600	95.7	34.6	0.117
0.65	72,500	67,300	92.8	34.5	0.115
0.82	72,000	69,000	95.8	35.7	0.116
1.66	70,000	68,000	97.2	33.8	0.117

Laminate Composition

Resin	Paraplex P-43 (Rohm and Haas) diluted with 10% styrene
Catalyst	2% Luperco ATC (Lucidol Div., Wallace Tiernan)
Reinforcement	12 ply, 181 glass cloth
Curing Temperatures	1 hour at 145°F., 1 hour at 245°F.
Pressure	Pressed to ⅛" stops
Laminating Procedure	Standard wet layup

Table 8. Relationship of Flexural Strength Properties of Phenolic Laminates to A-1100 Loadings on the Glass Cloth Reinforcement

Actual % A-1100		Avg. Flexural Strength, psi				
By Carbon Analysis	By Nitrogen Analysis	Room Temp. Dry	Tested at 500°F. After 100 Hours at 500°F.	Per Cent Retention	% Resin Content	Thickness Inches
—	—	69,500	13,200	19.0	28.2	0.112
0.10	0.08	83,300	45,900	55.2	27.0	0.104
0.19	0.27	82,200	43,200	52.6	28.1	0.109
0.41	0.39	80,600	51,900	64.0	29.2	0.114
0.73	0.76	77,900	54,500	69.0	31.9	0.118
0.92	0.96	82,500	52,300	63.4	25.2	0.110
1.4	1.6	84,300	48,500	57.6	29.4	0.111

Laminate Composition

Resin	V-204 (Plastics and Coal Chemicals Div., Allied Chemical Corporation)
Reinforcement	13 ply, 181 glass cloth
Curing Temperatures—	
"B" stage	3 minutes at 265°F.
Press cure	30 minutes at 290°F. (200 psi)
Postcure	1 day at 110°C., 1 day at 150°C., 1 day at 175°C. and 1 day at 200°C.
Laminating Procedure	Standard dry layup

These extraction tests, thus, did not explain why multi-molecular layers were needed. If anything, the ease of removal of the outer layers for these coupling agents and the tighter adhesion of the layers in contact with the glass would suggest that a monolayer would be superior in performance. This, of course, does not correlate with the results of laminate testing. Vapor phase treatment of the glass to achieve uniform monolayers would be an interesting way to study this further.

Electron Microscopy

A number of years ago, an attempt was made to utilize electron microscopy to study these coupling agents on glass, but because the fiber was opaque to the beam no success was obtained. Recently a new replica technique was developed in England° which appeared applicable to glass and development of this technique has resulted in some understanding of the need for high loadings. This new technique has shown that the excess loading is concentrated in capillary crevices between the individual filaments of a strand.

A single strand of heat-cleaned 181 cloth contains some 204 filaments of 5-8 microns diameter per filament, as shown schematically in *Figure 4*. These filaments are not tightly packed so that liquids or gases can penetrate to the inner surfaces. When a cloth woven from such strands is treated with one of the finishing solutions, the

° Bradley, D. W., *Nature*, 875 (1958)

Table 9. Four Hour Soxhlet Extraction of A-1100 Finished Cloths with Water

Test Number	Per Cent A-1100 Loading Before Extraction	Per Cent A-1100 Loading After Extraction	Per Cent of A-1100 Finish Removed
1	0.25	0.063	75.
2	0.38	0.063	84.
3	0.48	0.048	90.
4	0.73	0.11	87.
5	1.50	0.079	94.

Table 10. Attempts to Prepare High Volan A Loadings on 181/112 Cloth

Volan Cloth	Analysis			
	% Volan A			% Volan A
Nominal Loading and Method of Preparation	% Cr	Based on % Cr	% C	Based on % C
0.8% Volan A, heat set 5 minutes at 125°C., unwashed	0.229	0.53	0.104	0.52
0.8% Volan A, heat set 5 minutes at 125°C., washed one minute, dried two minutes at 125°C.	0.073	0.17	0.016	0.08
0.8% Volan A, heat set 20 minutes at 125°C., unwashed	0.246	0.56	0.083	0.41
0.8% Volan A, heat set 20 minutes at 125°C., washed one minute, dried two minutes at 125°C.	0.092	0.21	0.029	0.14

5 6

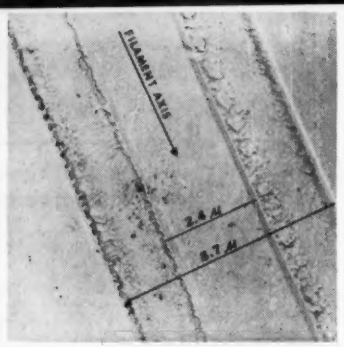


Figure 5. 80,960 X, blank glass cloth: Maximum roughness of unfinished filaments shown

Figure 6. 21,440 X, 1.6% A-1100 on glass cloth: Heavy strips of A-1100 finish are parallel to the filament axis at the intersections of filaments

solution on the glass strands tends to concentrate in the capillary channels formed at the intersections of the filaments. The result is that, although there is probably a fairly uniform polymer finish over all the filament surfaces, a major portion of the excess loading will deposit in the interfilament channels and appear as oversized agglomerates whose attachment to the substrate is not as secure as that of the smaller particles. This buildup has been observed with both phase and electron microscopes and is discussed in more detail below. Electron micrographs which show this effect are included.

The replica technique used in this work actually shows the glass surface and the finish configuration. The electron micrographs are obtained from replicas of individual filaments; the replicas are made by simultaneously shadow-casting the specimen with platinum and carbon and then "floating off" the replicated specimen onto hydrofluoric acid which in turn dissolves the glass strand away from the replica. The replica is then washed free of HF and fluorides with distilled water and "picked up" on an electron microscope grid which has been previously covered with a very thin film of Formvar. The grid and replica are then placed in the electron microscope, pumped down, scanned and photographed. The combined platinum-carbon gives good contrast without the loss of resolution due to "pile-up" on the specimen which occurs when metals of lower atomic numbers are used. The practical limit of resolution for these specimens was between 40 and 50 Å. The platinum-carbon vapor was directed onto the specimen from a point perpendicular (directly overhead) to the specimen rather than from approximately 45 degrees as is usually done for particulate matter. The reason for this is that the filament presents a curved surface to the platinum-carbon shower and in this way shadows are cast by the surface irregularities of the filament and imaged in position alongside the image of the surface irregularities. The filament axis and height and shape of irregularities can be inferred from these shadows, which appear as light spots on the positive prints.

Figure 5 shows an electron micrograph at 80,000 magnification on the surface of a portion of one strand of heat-cleaned 181 cloth and actually of a single filament. Note the extreme smoothness of the surface, which checks with the very low calculated roughness factor from surface area measurements. The parallel lines probably indicate where other filaments were in contact with the one shown before the strand was pulled apart and replicated.

Electron Micrographs With Aminoalkylsilane (A-1100)

The following three electron micrographs show the effect of capillary deposition for A-1100 and the effect of water extraction. *Figure 6* shows heavy strips of A-1100 resin running parallel to the filament axis. These strips, located in the channels between two filaments, represent an appreciable fraction of the loading. Observe that the distance between the strips is 2.4 microns and that the distance between the outer edges of the two strips is 5.7 microns. This is rational with our description of a glass strand composed of cylindrical filaments 5 to 8 microns in diameter. Notice also the much lighter loading between these strips. This will show up better at higher magnifications.

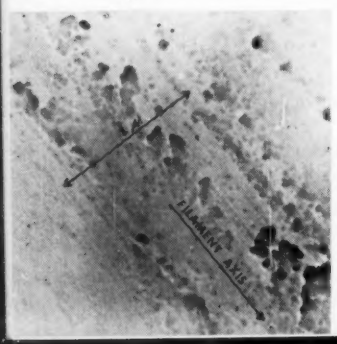
Figure 7 shows a smaller area of a filament from the same A-1100-finished cloth after it was extracted with water for four hours. The magnification in *Figure 7* is 80,960X compared with the 21,440X of *Figure 6*. Note that the A-1100 loading has been reduced from the 1.6% level of *Figure 6* to slightly less than 0.1% in *Figure 7* by the extraction with water. The distribution of *Figure 7* is also much more homogeneous.

Figure 8, an 80,960X magnification can now be advantageously compared with *Figure 9*. *Figure 8* was loaded with 0.1% A-1100 originally with no extraction and shows much poorer homogeneity than *Figure 7* with clearly visible concentration in the interfilament channel. This seems to explain why loadings greater than calculated monofilms are needed for optimum performance.

Electron Micrographs with Vinylsiloxane (A-172)

The following group of five electron micrographs shows similar effects for A-172: Loading is calculated using system presented below.

Figure 7. 80,960 X, A-1100 on glass cloth: Finish retained after 4 hours extraction of 1.6% loading with hot water; less than 0.1% loading left here



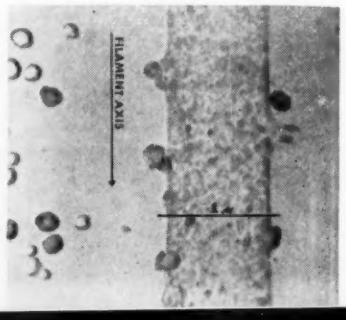


Figure 8. 80,960 X, 0.1% A-1100 on glass cloth: Heavy concentration in interfilament channels shown even at this low loading. Compare with figure 2 where loading was reduced from 1.6% to 0.1% by water extraction

Figure 9. 9,240 X, 0.5% A-172 on glass cloth inter-filament channel

Calculation of A-172 Loading from Electron Micrograph

1. Measure the length and width of the field on the photograph and calculate in square centimeters *the area* using the appropriate magnification factor.

2. Count the number of hemispheres of polymer in the field and measure their *diameter* using a focusing magnifier. If the hemispheres are roughly the same size, an average diameter can be used.

3. Calculate in cubic centimeters the *volume of the hemispheres* by multiplying the number of hemispheres times $2/3\ \pi\ r^3$. Do this for each size of hemisphere.

4. Calculate the *weight of the* $CH_2 = CHSiO_{3/2}$ by multiplying the total volume of the hemispheres times the *density* of the polymer, 1.2 g./cm^3.

5. Calculate the per cent A-172 according to the equation:

$$\frac{\text{weight in g. } 1.7 \times 10^3 \text{ cm}^2 \text{ surface area/g. x } 3.54^* \text{ x } 100}{\text{area of field in cm}^2} = \%\ \text{A-172}$$

Sample Calculation:

Table 10
66,500 X
1 mm = 0.015 micron

a. Field: 180 mm. by 177 mm.

Area: 180 mm. x 0.015 micron/mm. x 177 mm. x 0.015 micron/mm.
= 7.16 square microns or
7.16×10^{-8} cm.

b. Particle Count:

No. of Hemispheres	Diameter in Microns	Radius in Centimeters
5	3.0 mm x 0.015 = 0.045	2.2×10^{-6}
37	4.0 mm x 0.015 = 0.06	3.0×10^{-6}
2	5.0 mm x 0.015 = 0.075	3.8×10^{-6}
13	6.0 mm x 0.015 = 0.09	4.5×10^{-6}

* 3.54 ($CH_2 = CHSiO_{3/2}$) = A-172

c. Volume:

$5 \times 2/3 \times 3.14 \times (2.2 \times 10^{-6})^3 = 0.11 \times 10^{-15}$ cm^3
$37 \times 2/3 \times 3.14 \times (3.0 \times 10^{-6})^3 = 2.09 \times 10^{-15}$ cm^3
$2 \times 2/3 \times 3.14 \times (3.8 \times 10^{-6})^3 = 0.22 \times 10^{-15}$ cm^3
$13 \times 2/3 \times 3.14 \times (4.5 \times 10^{-6})^3 = 2.47 \times 10^{-15}$ cm^3
4.89×10^{-15} cm^3

d. Weight:

4.89×10^{-15} cm^3 x 1.2 g/cm^3 = 5.86×10^{-15} g.

e. Per cent A-172:

$$\frac{5.86 \times 10^{-15} \text{ g. x } 1.73 \times 10^3 \text{ cm}^2/\text{g. x } 3.54 \times 100}{7.16 \times 10^{-8} \text{ cm}^2} = 0.05\%\ \text{A-172}$$

Figure 9 is a low magnification (9,240X) picture of A-172 finish (0.47% loading). Notice how the deposit is concentrated towards the interfilament channel.

Figure 10 is a 66,500X magnification of a non-channeled area of a 0.03% A-172-loaded cloth, by chemical analysis. The loading, as calculated from the electron micrograph is 0.05%.

Figure 11 (21,440X) shows an interfilament buildup on a cloth whose average loading, by chemical analysis, is 0.26% A-172. The loading in the interfilament channel, calculated from the micrograph, is 2.43%.

Figure 12 shows, at 66,500X magnification, a specimen which has a 0.26% A-172 loading based on chemical analysis. The loading calculated from the picture is 0.19%.

Figure 13 shows a heterogeneous area of an A-172-finished filament from a cloth which was shown by chemical analysis to have an 0.6% loading. The calculated loading for the field shown in this plate is also 0.6%.

Electron Micrographs with the Methacrylato-Chromium Complex (Volan A)

Figure 14 shows interfilament buildup of Volan A-finished cloth before washing to remove excess salts; while *Figure 15* is a typical area of a Volan-finished cloth carrying 0.13% Volan A load.

Conclusions

We have shown that a "chemical bridge" mechanism for coupling agents between glass and resin seems to fit all the known facts of glass-resin laminate performance. We have shown that specific reactivity of a functional group on the coupling agent with suitable groups of the resin is important for optimum properties.

If a perfect monolayer of coupling agent could be applied to glass, it could not be seen or proven by the techniques described here. Considering the nature of the deposits as shown in the electron micrographs, the maximum roughness of surface which may be encountered in the blank and the 40 Å limit of resolution, it is impossible to interpret micrographs of finishes where the loadings are below 0.02%.

It is unlikely however, that such a smooth coating exists. First a typical electron micrograph (*Figure 10*) of low total loading of A-172 (0.03%) accounts for all the vinylsiloxane in the agglomerates, leaving none available for the postulated monofilm and, second, the performance data for laminates previously discussed suggests that the monofilm does not exist. Third, the conventional application from aqueous solution ensures that polymer forms before contact with the glass, leading to the visible agglomerates in the electron micrographs.

It is clear that a high proportion of the coupling agent may be found in the capillary spaces. The excess may be removed or redistributed by water or solvent extraction.

Extraction, however, is an undesirable added step in practical usage. The high degree of agglomeration suggests that techniques for putting monomers directly on the clean glass might yield films which might show superior properties. Solvent or vapor phase treatment would be of interest here and possibly of practical value if such improvements justified handling problems.

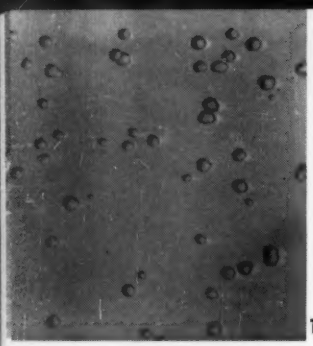
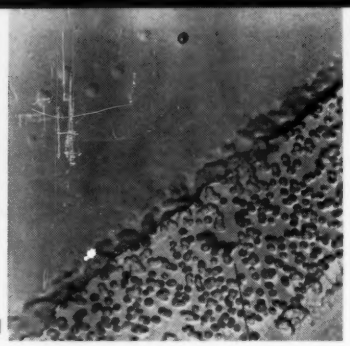



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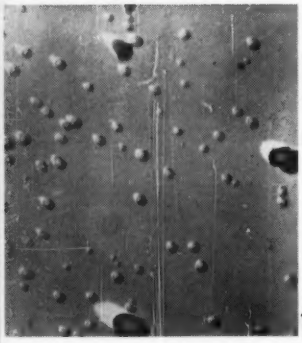
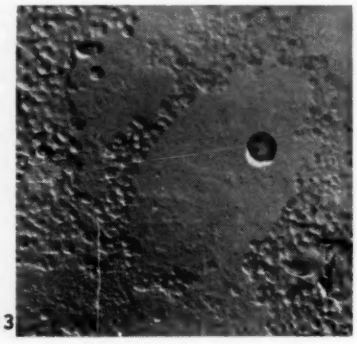
Figure 10. 66,560 X, A-172 on glass cloth:
Loading by chemical analysis 0.03%
Loading calculated from picture 0.05%

Figure 11. 21,440 X, A-172 on glass cloth:
Average loading by chemical analysis 0.026%
Calculated loading in inter-filament channel 2.43%

12 13

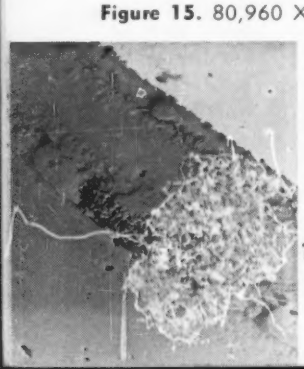
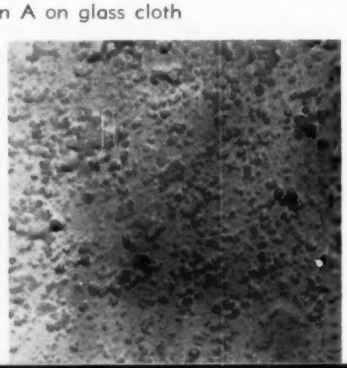
Figure 12. 66,500 X, A-172 on glass cloth:
Loading by chemical analysis 0.26%
Loading calculated from picture 0.19%

Figure 13. 80,960 X, water extracted A-172 glass cloth
Loadings by chemical analysis 0.6%
Loading calculated from picture 0.6%

This work also suggests that treatment of the individual filaments at the bushing with a "permanent" coupling agent would avoid this capillary buildup problem, as well as the heat-cleaning step and thus improve overall properties. This would mean, of course, that the problems of lubricant and binder would also have to be solved at this point. Electron microscopy would be a useful tool in such work as well as in study of improved finishes generally.

Figure 14. 21,440 X, 0.5 Volan A on glass cloth: Note buildup at inter-filament channel

Figure 15. 80,960 X, Volan A on glass cloth

14 15

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The Degree of Bonding Between Coupling Agents and Glass Filaments

. . *a study* . .

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Three approaches were used to study the degree of bonding between coupling agents and silica, type "E" (alumina borosilicate) and high modulus (beryllia-magnesia—silicate) glass. The strength of the chemical bond that exists depends upon the elements which make up the bond existing in the immediate surrounding area.

In the past five years, new formulations of glasses have been developed to obtain advantageous properties in laminates and resin-bonded glass filament composites. Silica or quartz in a spun or continuous filament has been used to improve the high temperature properties and beryllia-containing glass to develop an improved modulus or to obtain the desired stiffness in design for less weight per part. Type "E" glass is the present day standard for the fiberglass industry and, with slight variations, is supplied by all major producers in this field for every conceivable use.

The published information on the composition of these three glasses is given in *Table 1*. The silica is a twelve-end roving composed of approximately 50 continuous filaments per end, each filament in the order of 0.0004″ in diameter and covered with a starch-oil emulsion coating of unspecified composition. This roving was made by the Lamp Division of the General Electric Company, Cleveland, Ohio. The beryllia-containing high modulus glass was obtained from the Imperial Glass Company, Bellaire, Ohio, as a single-end strand (with a hot water applied starch emulsion) containing nominally 48 filaments, each filament 0.0004″ in diameter. The "E" glass was the standard commercial 150 1/0 product supplied as either an eight-end roving or single-end, but in all cases with type #630 (starch-oil) binder.

Surface Activity by Titration

A study on the surface activity of various fiberglass compositions was recently presented. (1) The background for this work is found in the colloidal chemistry studies of silica. (2, 3) The investigators of the latter reference show that modified silicate glasses may be characterized by an analysis of their chemical composition, their surface areas (via nitrogen or krypton gas adsorption), their degree of surface hydration, and by acid and base titrations to determine the number and strength of acidic and basic functional groups present on their surfaces. One of these authors (1) has contributed the surface area and acid-base titration results presented in this article.

These authors show that an acid-base titration curve will indicate the following classes of ions in solution: (1) no free acids or bases, but only neutral salts, when the titration curve is superimposed on the blank curve run on distilled water; (2) free strong acids or bases if the titration curve is displaced to the right or left, respectively, but having the same shape; and, finally, (3) the salt of a strong base with a weak acid or a weak base with a strong acid when the titration curve is displaced to the left or right, respectively, as with the strong acids and bases. There will be an additional discontinuity or break located at a pH value approximately equal to the dissociation constant (pKa) of the weak acid or base, respectively. The number and type of acidic surface groups can be determined by a computation based on the moles of base titrated between pH 2.5 to 7.5. The number of silanol groups per square millimicron of surface was computed from another equation (1) using the c.c. of base required to titrate from pH 7.5 to 9.25.

$$n = \frac{0.6 \times \text{c.c. of base}}{SA}$$

Table 1. The Recorded Compositions of Silica, Type "E" and Imperial #905 HM Glasses

(No Sizes Applied)

Component	Silica[1] %	"E"[2] %	Imp. #905[3] %
SiO_2	99.97	54.5	48.0
Al_2O_3	0.015	14.5	0
CaO	0.0032	17.0	11.85
B_2O_3	0.00	8.5	8.0
BeO	0.00	0.0	8.0
Li_2O	0.00	0.0	6.0
V_2O_5	0.00	0.0	4.0
MoO_2	0.00	0.0	2.0
MgO	0.00	4.5	8.15
TiO_2	0.00	1.0	4.0
Na_2O	0.0022		0.0
K_2O	0.0007		0.0
Fe_2O_3	0.0010		0.0

[1] The silica analysis given as typical for production by Lamp Division, General Electric Co., Cleveland, Ohio.
[2] The "E" glass analysis is listed in a Symposium Preprint on High Modulus Glass by WADD, Dayton, Ohio, October 12, 1960.
[3] The Imperial #905 formulation is that given in Report to the Department of the Navy by Imperial Glass Co. dated 15 January 1960.

$$\left[\left(\text{antilog} \frac{12.08 - 0.74 \log [Na^+] - pH}{3.47} \right) + 1 \right]$$

n = no. of silanol groups per square millimicron of surface.
SA = the surface area as determined by nitrogen-krypton gas adsorption.
$[Na^+]$ = the activity of the sodium or other monovalent cations in the system.
pH = the negative logarithm of the hydrogen ion activity.

The thought is advanced that the more complex glass formulations have the silica structure that behaves as a weak acid but also have on the surface another structure based on borosilicates and aluminosilcates. The non-silica structure may be removed in "E" glass almost completely by strong acid leaching, at elevated temperatures in certain commercial processes, therefore it would appear that these two structures are entwined although independent. Ten grams of glass strands in heat-cleaned state are dispersed in 150 c.c. of 4.0 N NaCl. Prior to titration they are chopped to relatively fine lengths by mixing with distilled water in a Waring Blendor and dried at 110°C. in an oven. The pH of the salt solution of the glass fiber is adjusted to pH 2.5 by adding 0.001 N HCl and then titrated upward to 9.25 by adding 0.001 N NaOH. The NaCl acts as a supporting electrolyte in these titrations to sharpen the breaks in the curve obtained from the titration of polymeric surface acidic groups. The structure of the silica has been carefully determined as contributing eight sites per square millimicron. For calculations comparing the number of more strongly acid sites a comparison or ratio may be made with those of the silica structure. This approach will be used in the presentation of data in this paper. The mild surface leaching acid used was 0.01 N HCl but otherwise the procedure was the same as described above as performed by Dr. Yates.

Electron Micrographs

A technique for taking electron micrographs of glass filament surfaces has been recently described. (3) According to this paper, the electron micrographs are obtained from replicas of the individual filaments and show the glass surface and finish configuration. The replicas are made by simultaneously shadow-casting the specimen with platinum and carbon, then "floating off" the replicated specimen into hydrofluoric acid which dissolves the glass strand away from the replica. Using distilled water the replica is then washed free of HF and fluorides and "picked up" on a very thin film Formvar-covered electron microscope grid. The grid and replica are then placed in the electron microscope, pumped down, scanned and photographed. The combined platinum-carbon gives good contrast and resolution down to a lower limit of 40-50 Å. Since the filament already presents a curved surface, the platinum-carbon "shower" was aimed downward from directly overhead to coat the surface irregularities in a manner to cause a shadow. The filament axis and the height and shape of irregularities can be inferred from these shadows which appear as light spots on the positive prints.

One of the authors of the above-mentioned electron microscope study paper has furnished additional electron microscope photographs of the rovings and strand being studied here. Interpretation of these later photographs must be tentative because an insufficient number were taken on the area examined in comparison to the total area available.

Heat Cleaning and Finishing

A method is given (3) for continuously heat-cleaning and finishing 150 1/0 continuous "E" glass filament strand and making 18" diameter epoxy resin-bonded continuous filament hoops. The coupling agents studied are all applied with various solvents to the continuously heat-cleaned glass surface. All strength and modulus testing was in flexure with 4-point loading (*Figure 1*). It was noted that all 4" long specimens, whether on the tensile or compressive side, initially failed in shear at or near the glass in the interface area. If it was in compression the failure was abrupt and under or between the two centrally located ¼" loading bars. If the failure was in tension along the bottom of the piece, it always appeared in the one-half inch area under the central loading bars. A portion of a glass strand would separate or shear away from the composite, load independently of the composite and break. The tensile side failures are initiated by a shear failure at or near the interface and are gradual, showing a jagged level or gradually rising stress line on failure. Specimens of hoops made from irregularly tensioned strand, or of hoops having a poor resistance to moisture attack, usually failed in interlaminar shear, that is, along the neutral axis halfway between the two curved surfaces.

All the work presented in this article was performed with the same bonding resin as in reference (5), namely,

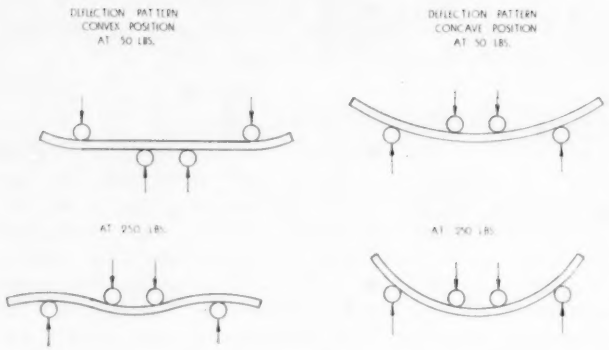


Figure 1. Application of four point load in flexure. The dry convex and concave flexured samples are averaged to give the recorded result. The samples boiled for 12 hours are tested wet in the convex position. An adjusted figure is calculated by dividing the wet convex and multiplying by the dry average

100 parts Epon 828, 91 parts Nadic methyl anhydride and 0.3% N,N-dimethyl benzyl amine as catalyst. Curing of the hoops was always 16 hours at 250°F. followed by 4 hours at 360°F. to, if anything, overcure the resin and eliminate cure as a problem.

It is the purpose of this article to present a series of results gathered on G. E. continuous filament quartz roving, continuous Type "E" glass roving and continuous Imperial #905 High Modulus glass roving by each one on the three techniques described above.

Presentation of Data

Into the continuous heat-cleaning and finishing line illustrated in *Figure 2* A and B were fed one end of each of three rovings roughly equivalent to eight strand ends "E" glass 150 1/0. Each had about 2% of a starch or starch-oil size to be removed. While continuously passing through the tube under the infrared heater at 1175°F. for 8-12 seconds in an oxygen-enriched atmosphere, the organic materials are removed down to a residual amount approximating 0.03% organic solids or less. For vapor phase treatment *(Figure 2A)* with γ-amino propyl triethoxy silane (A-1100)*, the rovings are then passed through a box of moisture-treated air at 300-400°F. and into another box of dry A-1100 vapor at approximately 200°F. and a final box at 400°F. Residence time in each box is about two seconds. To apply the chrome complex (*Figure 2B*) containing an epoxy-reactive organic acid group (Volan E)** a 2% aqueous solution of the commodity was adjusted with a 1% ammonia solution to a pH of 5.3 before use and constantly adjusted during use to hold this pH value. The chrome complex solution treated strand was dried for approximately three seconds under an infrared heater in contact with the flat surface of a chrome-plated wheel heated to 250°F. Both the silane (A-1100) and chrome complex (Volan E) treated rovings were then wound on spools at a tension of approximately 200 grams per roving end. Heat-cleaned samples approximating 40 grams (2 spools) of each roving were collected for examination.

* A-1100, Union Carbide's gamma-aminopropyltriethoxysilane.
** Du Pont's chrome complex with an epoxy-reactive organic acid group.

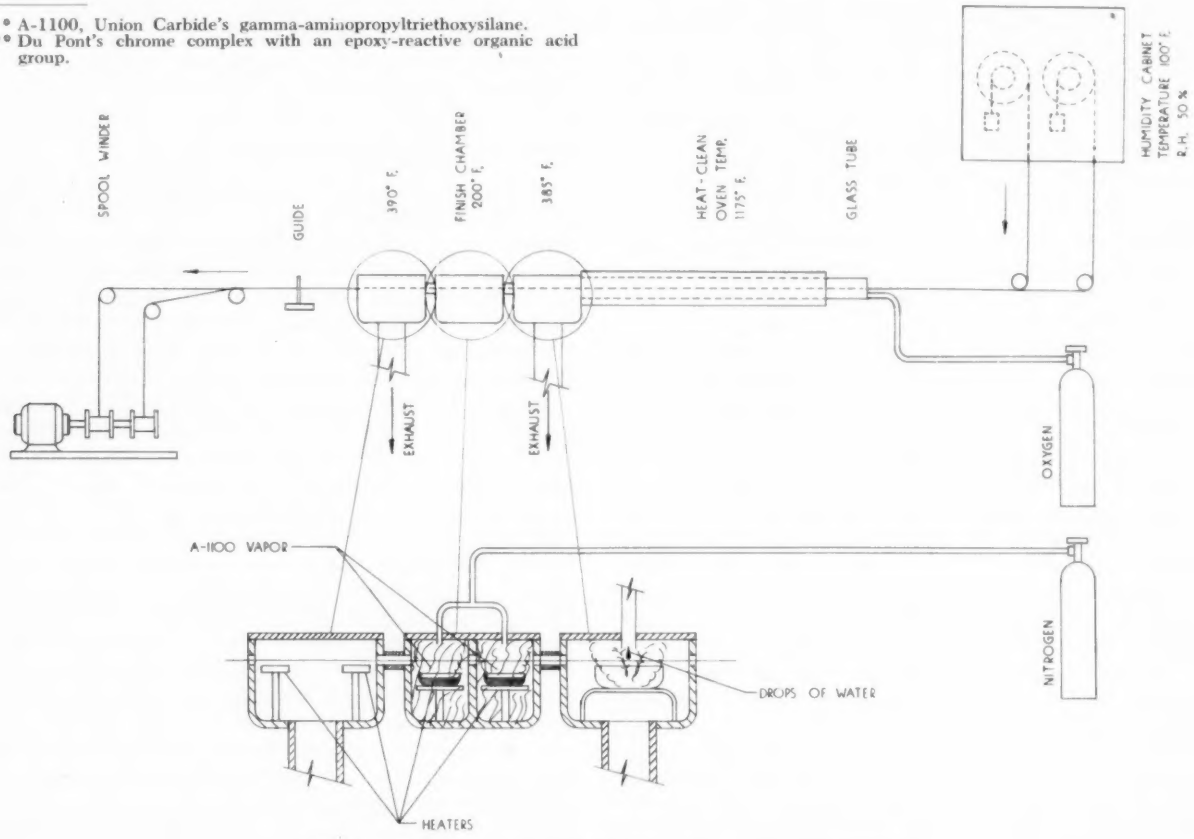


Figure 2A. Heat cleaning and finishing line (vapor application)

Glass Surface Properties

The bare glass was found to have the following characteristics:

	Surface Area by Nitrogen or Krypton Absorption in m^2/g	Number of Reactive Sites Per Square Millimicron pH 2.5-4.0	pH 4.0-7.5	pH 7.5-9.25
"E" Glass	0.106	0	4	8*
Silica	0.198	0	4	8*
High Modulus Glass (HM)	0.232	6	3	8*

The surface areas of each glass show the same order of magnitude indicating that each is without appreciable porosity larger than the diameter of the gas molecules used. The continuous silica fibers appear not to be pure silica on the surface but contaminated with possibly some alkali alumino silicate such as $NaAlSiO_4$ and give a reactivity at pH 4.0-7.5. "E" glass, on the other hand, undoubtedly has borosilicate in addition to alumino silicate groups with alkali cations to counterbalance their negative charges. (1) (6) In any case, it is interesting to note that a silica fiber surface may become contaminated by a very small quantity of impurity** in bulk having a small atomic volume tending to concentrate at the surface to lower the surface energy and also the total free energy of the glass. Here it could react with an alkali metal migrating from the size to the surface. Very likely this concentration of impurity on the silica surface occurs during the forming process. In any case, the surface silanol activity is changed and the G. E. almost pure silica glass approaches the surface characteristics of "E" glass. Titration of the beryllia-containing high modulus glass shows two distinct breaks in the curve, one in the pH 4.0-7.5 range showing the presence of acid groups having the strength of acetic to carbonic acid, like lithium borosilicate, for example. The presence of borosilicates (8% in the bulk formulation) is likely to be the major contributor to this mildly acidic break. However, it is the more strongly acidic (equivalent to that of formic) break that appears to change the character of this glass surface. Very possibly, the contributing factor is the beryllium ion having a small atomic volume and comparatively high nuclear charge. Beryllium contains twice the number of electrons for sharing as lithium, therefore the reactivity of the surface silica network surrounding any one beryllium atom can be reduced by the polarizing action of the beryllium. It affects drift of the electron cloud around the silanol groups.

* The figure for "n" in equation 1 was assumed to be that for a standard silica structure—8 sites per square millimicron.

Electron Micrograph Studies

The electron micrograph study of the glass surface may be seen by examining in turn *Figures 3-6*, inclusive. *Figures 3 and 4* are taken with permission of Messrs. Sterman and Bradley (4). In this reference the authors state that this photograph at 80,960 magnifications is the surface of a filament of a twisted and plied strand of batch heat-cleaned Style 181 cloth. The mat finish pattern is characteristic of a heat-cleaned glass surface and indicates that this filament surface, as compared to other materials, is remarkably smooth. The linear and aggregate markings in this micrograph, these authors say, may be minute residues of starch-oil size that were between two closely packed filaments during heat-cleaning.

In the second electron micrograph, *Figure 4*, there is shown at the same magnification as above the effect of depositing 0.1% A-1100 on the surface of a filament in a twisted strand of Style 181 fabric and in the capil-

** Such as element aluminum in whose outer shell the removal of an electron requires a particularly low energy (8).

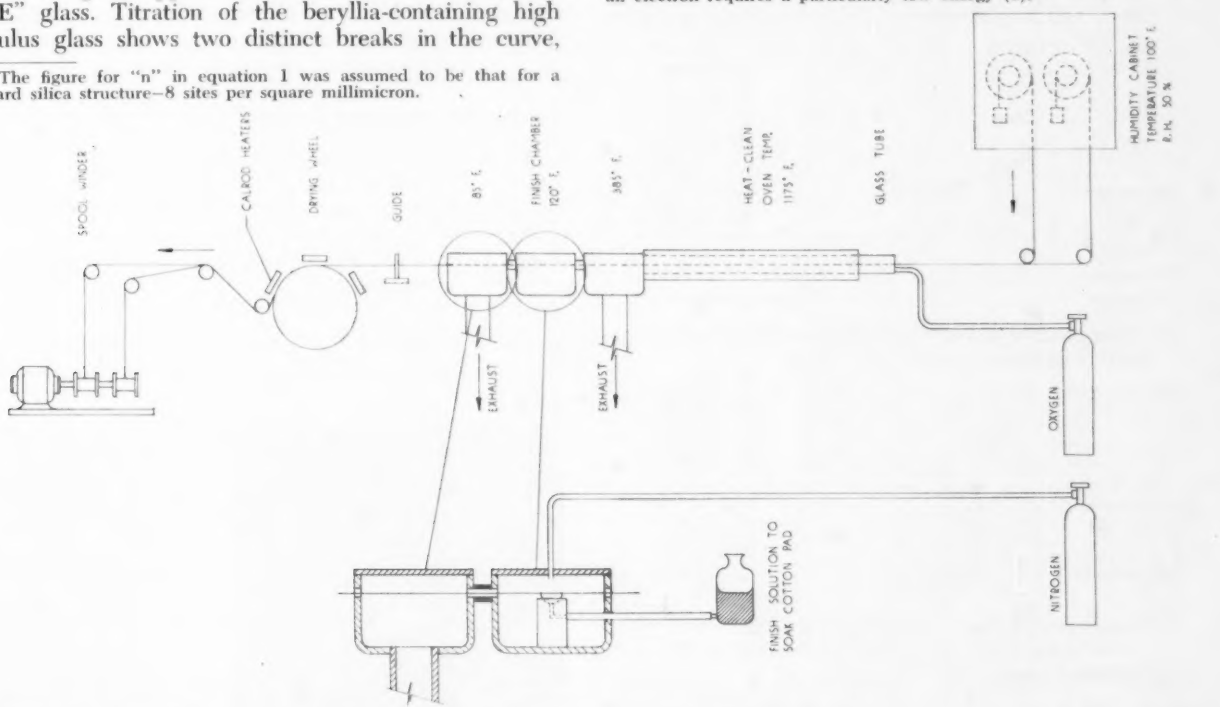


Figure 2B. Heat cleaning and finishing line (solution application-chrome complex on roving)

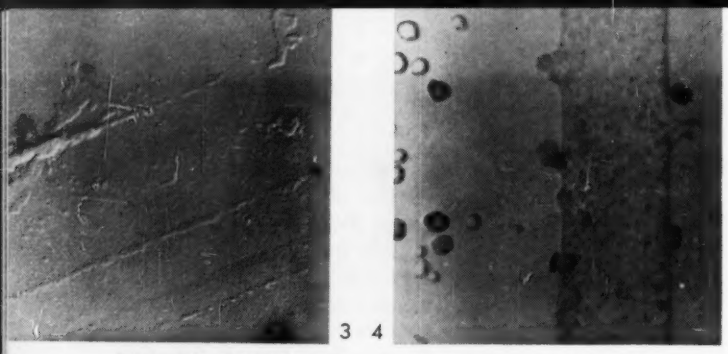


Figure 3. 80,960X: The surface on an "E" glass filament from a twisted and plied strand of batch heat cleaned cloth. This photograph shows a condition of maximum roughness for such a surface

Figure 4. 80,960X: Two adjacent "E" glass filaments of batch heat cleaned, finished, twisted and plied strand in a fabric. Loading on the cloth is 1% by weight. Note the heavy concentration of amino alkyl siloxane in the inter-filament channels

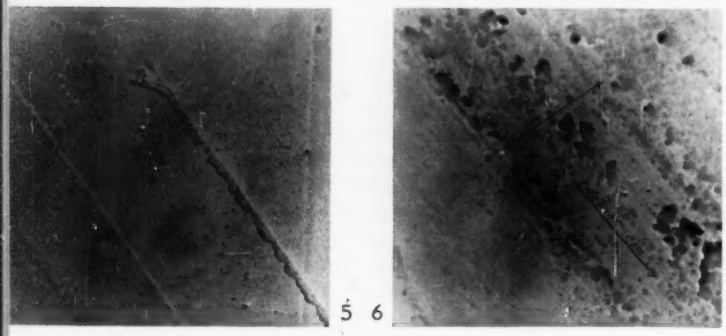
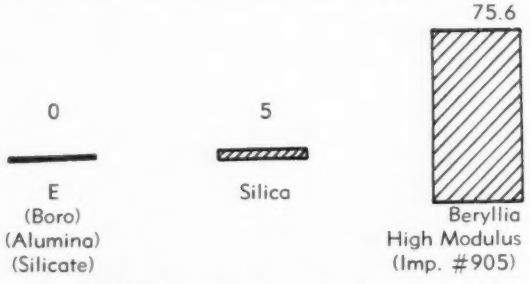
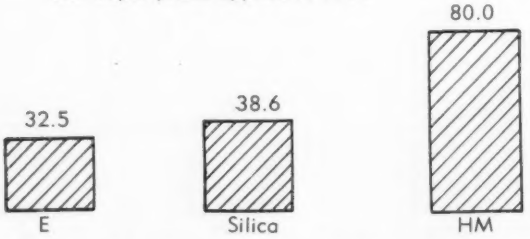


Figure 5. 82,400X: The surface of an "E" glass filament heat cleaned in oxygen-enriched air then exposed to humid air and then to A-1100 vapor (part of a strand of 8-end roving)

Figure 6. 82,960X: The surface of an "E" glass filament of batch heat cleaned glass cloth that has been finished with a high concentration of A-1100 (1.6% solids loading) then immersed in hot water for four hours in a Soxhlet Extractor. Less than 0.1% solids remained on fabric after treatment



A. Heat-cleaned in oxygen-enriched air and finished with vapor phase applied A-1100



B. Heat-cleaned in oxygen-enriched air and finished with Volan E applied as 2% commodity in NH_3 adjusted water to pH 5.3

Figure 7. The loss of flexural strength of a hoop during 12 hours in boiling water as a function of the glass formulation

laries between these filaments. The actual areas of contact between the A-1100 and the glass are believed to be the series of button-like agglomerates shown on the smooth areas. Note that a considerable portion of the smooth areas appear uncovered and that the agglomerates to the left of the bridging or roughened portion of the photograph cover about 1% of the surface. *Figure 5* shows two filaments chosen at random from the "E" glass roving continuously heat-cleaned in oxygen-enriched air, surface treated with humid air, then treated with A-1100 vapor and heated to 400°F. for two seconds. A sample of this cleaned and finished "E" glass roving was analyzed by Mr. Sterman's group using a Kjeldahl nitrogen analysis for deposited A-1100. A nitrogen value found indicated about 0.03% A-1100 was deposited on the glass. This is equivalent in weight to approximately a monolayer of A-1100 on the filament surface. (4) Although an insufficient number of micrographs were taken to be certain whether these random views are typical for this treatment, it may be stated that they show a remarkable agreement and would appear to indicate a thin, uniform layer of A-1100 on the glass surface. It must be remembered that resolution of the micrograph is not certain under 40-50 Å.

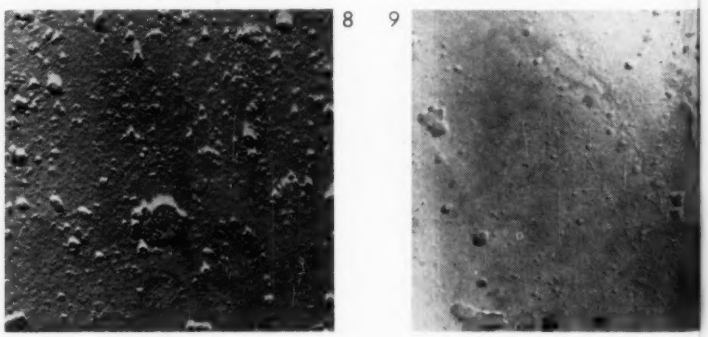
It is also of interest to examine the electron micrographs (3) of samples of batch heat-cleaned glass cloth, heavily coated with 1.6% A-1100 applied from aqueous solution and boiled for 4 hours in hot water in a Soxhlet extractor. At the end of the cycle less than 0.1% A-1100 was left on the surface of the fabric (*Figure 6*). This micrograph may be compared with that taken of the continuous heat-cleaned, vapor applied A-1100 coated "E" glass roving described above after it had been given a like hot water treatment for 4 hours (*Figure 8*). It is certain that these two micrographs show that the residual and possibly rearranged amino alkyl siloxane is different in each of these two cases, aqueous application and vapor phase treatment.

Properties in Resin-Bonded Composites

To determine the reactive flexural strength and modulus of these three glasses, Type "E", silica and high modulus, hoops 18" in diameter were made of rovings

Figure 8. 82,400X: The surface of a continuous heat cleaned "E" glass filament exposed to humid air, finished in A-1100 vapor and then exposed to hot water in a Soxhlet for four hours

Figure 9. 82,400X: The surface of heat cleaned "E" glass filament exposed to humid air, finished in epichlorohydrin vapor



continuously heat-cleaned in oxygen-enriched air and finished with vapor phase A-1100 or a 2% commodity aqueous solution of Volan E adjusted with 1% ammonia to pH 5.3 (*Table 2*). The relative losses in dry strength during 12 hours of boiling are shown in *Figure 7*. It was difficult to sufficiently tension the silica roving to get the same volume of glass content as the other two formulations.

By studying some other data collected on "E" and the Beryllia High Modulus Glass, some light can be shed on the probable source of the difficulty in the beryllia type formulations. *Table 3* contains this data. To commence with Section I of this table it may be seen that the dry flexural strength and modulus of a hoop may be raised by obtaining a more even tension of the strands as wound on the mandrel. However, although the statistics improve and the glass content increases, the strength loss on boiling remains about the same, in this case, negligible.

In another recently published work (7), the authors showed that epichlorohydrin appeared to react with the surface of Type "E" fiberglass. Section II of *Table 3* shows the results of vapor phase treating with epichlorohydrin. By ignition the pickup on the strand was 0.08%. *Figures 9* and *10* show electron micrographs of a filament of the treated strand. It may be presumed that, since this surface is distinctly different from a heat-cleaned surface (*Figure 3*), that some epichlorohydrin has been deposited. Gutfruend's and Weber's work previously referenced would support the belief that the epichlorohydrin has reacted with that surface.

The epichlorohydrin, by the time the coated strand has been fully reacted in the epoxy-resin-bonded hoop, forms a link to the glass, by virtue of a reaction of the chloride end with the surface silanol groups of the glass (and releases HCl as a by-product), and another link to the resin by virtue of a reaction of the epoxide end of this molecule with the anhydride hardener in the epoxy resin formulation. In another paper (5) it is shown that a glycidoxy group substituted for the amine group in

Table 2. A Comparison of Continuously Filament Wound 18" Diameter Hoops, 0.225" Wide X 0.125" Thick of Silica, E and High Modulus Glass Roving Bonded with Bisphenol Base Epoxy and t-Amine Catalyzed Nadic Methyl Anhydride

Hoop No.	Glass Type	Glass Content, % Wt/Volume	Flexural Strength $\times 10^3$ psi		Flexural Modulus $\times 10^6$ psi	
			Dry	12 Hr. Boil	Dry	12 Hr. Boil
Continuously heat-cleaned in oxygen-enriched air						
372	Type "E" Glass Roving	83.7/70.8	178.3	194.6	8.09	8.65
373	Type "E" Glass Roving	84.3/71.4	174.0	169.8	7.97	8.33
Average	Type "E" Glass Roving	84.0/71.1	176.2	182.2	8.03	8.49
	Loss of strength on boiling—0%					
383	G.E. Continuous Silica Roving	75.8/63.2	181.1	171.7	6.86	6.84
	Loss of strength on boiling—5.2%					
389	Imperial #905 HM Glass Roving	85.4/72.0	228	49	11.00	9.50
390	Imperial #905 HM Glass Roving	86.9/74.9	234	62	10.80	9.80
Average	Imperial #905 HM Glass Roving	86.2/73.5	231	56	10.90	9.65
	Loss of strength on boiling—75.6%					
B—Finished with Volan E applied from 2% commodity aqueous solution adjusted to pH 5.3 with 1% ammonia						
369	Type "E" Glass Roving	84.5/71.6	220.2	148.5	8.38	7.87
370	Type "E" Glass Roving	84.6/71.7	214.4	145.7	8.37	7.73
Average	Type "E" Glass Roving	84.6/71.7	217.8	147.1	8.38	7.80
	Loss of strength on boiling—32.5%					
371	G.E. Continuous Silica Roving	76.9/64.5	193.3	108.5	6.72	6.88
374	G.E. Continuous Silica Roving	76.7/64.2	177.5	99.2	6.75	6.58
Average	G.E. Continuous Silica Roving	76.8/64.4	185.4	103.9	6.74	6.67
	Loss of strength on boiling—38.6%					
367	Imperial #905 HM Glass Roving	83.5/69.0	238.0	43.3	10.26	8.75
368	Imperial #905 HM Glass Roving	84.3/70.3	239.4	50.0	10.37	9.65
Average	Imperial #905 HM Glass Roving	83.9/69.7	238.7	47.7	10.32	9.20
	Loss of strength on boiling—80.0%					

Table 3. A Comparison of Continuously Wound 18" Diameter Hoops, 0.225" Wide X 0.125" Thick of "E" and Imperial #905 High Modulus Glass Roving and Strand Bonded with Bisphenol Base Epoxy and t-Amine Catalyzed Nadic Methyl Anhydride

Section I.

The Effect of Tension on Flexural Strength and Modulus Properties: "E" Glass #630 Binder, Continuously Heat-Cleaned in Air + O_2, Finished With A-1100 in Vapor Phase

Glass Content, %	Flexural Strength $\times 10^3$ psi		Flexural Modulus $\times 10^6$ psi	
Wt/Volume	Dry	12 Hr. Boil	Dry	12 Hr. Boil
A. Single Tensioned End Hoop Construction				
87.4/76.5	245.0	240.5	8.46	9.22
B. Eight End Tensioned Roving Hoop Construction				
84.0/71.1	176.2	182.2	8.03	8.49

Section II.

The Effect of Using a Coupling Agent With a Strong Water-Resistant Bond, $-\overset{|}{\underset{|}{Si}}-O-\overset{|}{\underset{|}{Si}}-O-$, to "E" Glass vs That With a Water Attackable Bond, $-\overset{|}{\underset{|}{C}}-O-\overset{|}{\underset{|}{Si}}-O$ or γ-Amino Propyl Triethoxy Silane vs Epichlorohydrin as Glass-Reactive Agent

Glass Content, %	Flexural Strength $\times 10^3$ psi		Flexural Modulus $\times 10^6$ psi	
Wt/Volume	Dry	12 Hr. Boil	Dry	12 Hr. Boil
A. Vapor Phase Applied Epichlorohydrin to Glass Strand Heat-Cleaned Air + O_2				
87.6/76.8	222.0	Fell Apart	8.68	Fell Apart
B. Vapor Phase Applied -Amino Propyl Triethoxy Silane to Glass Strand Heat-Cleaned in Air + O_2				
87.4/76.5	245.0	240.5	8.46	9.22

Section III.

The Effect of Applying A-1100 in Various Manners to Glass Strand

Solvent	Glass Content, % Wt/Volume	Flexural Strength $\times 10^3$ psi		Flexural Modulus $\times 10^6$ psi		Loss of Strength 12 Hr. Boil
		Dry	12 Hr. Boil	Dry	12 Hr. Boil	
A. Starch-Sized "E" Glass Strand Continuously Heat-Cleaned in Air + O_2; Applied A-1100						
1% Water	84.9/72.3	249.2	229.2	8.53	8.54	8.2%
1% Dioxane	86.9/75.8	240.5	208.6	8.63	8.36	13.4%
1% Toluene	88.1/77.6	268.7	198.0	9.19	8.84	26.4%
Vapor Phase	87.4/76.5	245.0	240.5	8.46	9.22	1.5%
Bushing 10% Water*	82.5/69.0	195.0	188.0	7.62	7.68	4.0%
B. Imperial #905 HM Glass Strand						
1. Starch-Sized, Heat-Cleaned in Air + O_2; Applied A-1100						
1% Water	82.5/67.8	226.0	111.0	9.36	9.48	50.8%
Vapor Phase	86.2/73.5	231.0	56.0	10.90	9.65	75.8%
2. Sized With A-1100 in Water at the Bushing						
Bushing 7.5% Water*	85.7/72.9	248.0	109.0	10.17	10.14	56.0%

* No heat-cleaning

A-1100 will react with this same epoxy resin formulation almost as efficiently as A-1100 when this glycidoxy silane coupling agent has been deposited in a similar manner on the glass strand as the A-1100. There is, therefore, every reason to believe that the epoxy resin formulation has bonded to the epichlorohydrin on the glass fiber surface. However, the carbon-oxygen-silicon bond is too weak to resist the stress applied when the resin is swollen by water, although strong enough to resist heat without applied stress to 350°C. Thus, the bond is fractured by the small quantity of water adsorbed into the epoxy resin. This experiment lends evidence to the belief that low stress rupture bonds can be formed with the glass surface silanol groups by reacting the silanol

to form Si-O-C-bonds that tend to share electrons rather than form an ionic bond. On the other hand, it would appear that the A-1100 does form Si-O-Si bonds with the silanols on the glass fiber surface to liberate C_2H_5OH when applied from vapor phase or from anhydrous solvent, and to liberate HOH when applied from water solution. If a bond weakness can happen as illustrated, it is not unreasonable to surmise that the rapid loss of strength of the bond to the Imperial beryllia-containing high modulus glass in resin-bonded hoops is due to an element located in the surface silica lattice that has a strong proton drawing character and that this force would reduce the tendency of the glass surface silanols to form a high stress-resistant bond. Beryllium due to its low atomic volume and high ionic charge is the most likely element in the high modulus formulation to create this difficulty.

In Section III of *Table 3*, a presentation is made of various methods of applying A-1100 to Type "E" and beryllia-containing glass filament surfaces and the flexural strength and modulus results of epoxy-resin-bonded hoops cut up and tested both dry and after 12 hours in boiling water. Note that the "E" glass and high modulus glass substrates separate the strength results into two categories. The "E" glass applications have a range from 1.5 to 26.4% loss while the high modulus applications have a range from 50.8-75.8% loss of flexural strength properties due to 12 hours immersion in boiling water. To help in comparing the "E" glass hoops examine the electron micrograph in *Figure 11*. Compare this micrograph with those of *Figures 3* and *4*. *Figure 12* shows the surface configuration of two adjoining filaments that have been continuously heat-cleaned in oxygen-enriched air and finished with a 1% concentration of A-1100 in water. The loading was approximately 0.5% solids. The brilliantly shadowed strip running across the picture is a bridge of A-1100 across the inter-filament channel. Compare with the micrographs in *Figure 5*, the vapor coated A-1100 "E" glass surfaces. Note that the expanse of mat surface appearing in *Figure 11* is characteristic of the heat-cleaned surface of *Figure 3* and that the vapor-treated surfaces of *Figure 5* appear to have a much more complete coverage of the coupling agent. The deposition of the A-1100 from dry toluene solution on "E" glass, not illustrated here, has much the same appearance as the deposition shown on *Figure 11*, although the chemical reaction to form the deposit must be different. From water solution, the A-1100 in coating filaments of a strand bond that strand together by bridging the filaments are shown in *Figures 11* and *12*. *Figure 13* shows that these bridges can be more than three microns across and would tend to give low glass loadings (in this case, 84.9% by weight, 72.3% by volume) in the hoops. The bushing-applied A-1100 from a 10% concentration in aqueous solution must have caused even wider filament channels and longer bridges to give the lower glass content (82.5% by weight, 69.0% by volume). From dry toluene or dioxane solution, no bridges are formed and the pick-up of solution is much reduced (0.5% for water vs 0.14% for toluene solids on the

Fig. 10. 82,400X: Another view of surface described in Figure 9.

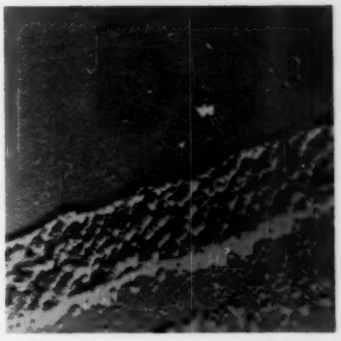


Figure 11. 82,400X: The surfaces of two "E" glass filaments and the bridge of aminoalkyl siloxane between them. As part of a strand they have been continuously heat cleaned and finished with a 1% solution of A-1100 in water

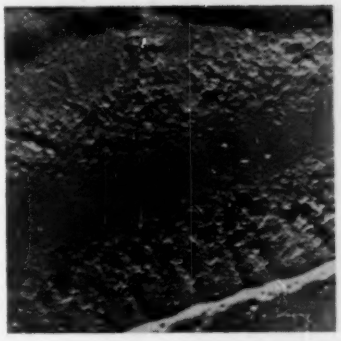


Figure 12. 82,400X: The surface of an "E" glass filament and a wide bridge of amino alkyl siloxane treated as the sample in Figure 11

Figure 13. 82,400X: The surface of two adjacent filaments of high modulus glass and the bridged area of amino alkyl siloxane between them. The filaments as part of a strand were continuously heat cleaned in oxygen enriched air and finished with a 1% solution of A-1100 in water

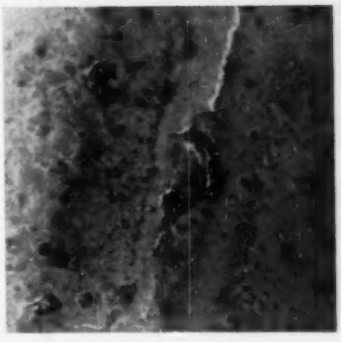


Figure 14. 82,400X: The surface of a filament and a large portion of a bridged area of amino alkyl siloxane treated in similar manner to sample in Figure 13

Table 4. Loading of Strands of "E", Silica and High Modulus Glass With A-1100 Applied from a 1% Solution in Water

	Percent A-1100 as Applied	Percent A-1100 After 4 Hours Soxhlet Extraction in Hot Water
1. G.E. Silica Glass Roving, Continuously Heat-Cleaned in Air + O_2	0.50 ± 0.05	0.06 ± 0.02
2. "E" Glass-150 1/0 Strand Continuously Heat-Cleaned in Air + O_2	0.45 ± 0.05	0.03 ± 0.02
3. Imperial #905, High Modulus Glass, Strand, Continuously Heat-Cleaned in Air + O_2	0.55 ± 0.05	0.02 ± 0.02
4. Heat-Cleaned as Above But Not Finished (1)	nil	—
5. Heat-Cleaned as Above But Not Finished (2)	nil	—
6. Heat-Cleaned as Above But Not Finished (3)	nil	—

The analysis for A-1100 was determined on nitrogen content by modified Kjeldahl method.

strand at 1% A-1100 concentration in solution). The bridging is believed due to the deposition of a partially chain extended but water soluble amino alkyl siloxane formed from the hydrolyzed A-1100.

A Mechanism for Bonding Resin to Finish to Glass

Since *Figures 4, 11* and *12* imply that the surface of a heat-cleaned A-1100-water finished "E" glass filament strand has comparatively wide uncoated areas, and the fact that laminates or continuously filament wound specimens (*Table 2*, Section IV) have high resistance to boiling water, it is necessary to consider a possible mechanism for bridging over the unreactive sites on the glass surface. In excess of A-1100 (4) can be removed from the finished glass surface through direct contact with hot water within a four-hour period. However, there will be a residue left on the glass, whether it be Type "E", silica or high modulus, of 0.02% to 0.06%, a value averaging a weight of one to two monolayers in thickness (See *Table 4* for this data, the work done by Silicones Division of Union Carbide Corporation). In the hoops boiled for 12 hours, the amino alkyl siloxane deposited from the water solution must have been penetrated in depth during lay-up by the laminating epoxy resin and the bisphenol-base diepoxide reacted with all or almost all the amino groups present and so insolubilize the siloxane in water. Although it would seem that an A-1100 deposition from dry toluene solution, due to less competition for sites from a non-polar solvent, should cover more sites on the glass surface than from water, it would appear from the data and micrographs that the deposition of A-1100 from the toluene solution does not cover appreciably more sites than the A-1100 applied from water. Since the individual agglomerates were less bulky, however, there was not the *in-depth bonding* into the epoxy resin of the amino alkyl siloxane network in the case of the toluene-applied A-1100 and this could account for the greater weakness (− 26.4%) displayed when a strain was induced on the surface site-bridging links by the swelling of the resin. The A-1100 deposited from dry dioxane did have polar solvent competition, but initially the dioxane solution, due to its polar nature, picked up from the pad to a greater degree and, therefore, deposited more solids on the surface to get greater in-depth tie-in with the amino alkyl siloxane network than from toluene, although not to the degree obtained from water solution. As the average glass-surface-site-spanning distance increases, the chance that a glass-finish bond will be able to take the strain induced by resin swelling becomes more problematical. It is also likely that the number of bonds available to transfer stress to the glass will be less.

While the site spanning mechanism appears to explain the differences induced by various methods of applying the A-1100, it is inadequate to explain the disparity between the flexural strength loss on boiling of high modulus glass vs "E" glass. However, by obtaining a more favorable build-up of coupling agent for in-depth bonding on the high modulus glass filament surface, it would appear that a degree of improvement in boiling resistance can be induced (*Table 2*, Section IV). *Figures 13* and *14* are electron micrographs of the surfaces of the Imperial #905 high modulus glass filaments in a strand. These strands have been continuously heat-cleaned in oxygen-enriched air and finished with a 1% solution of A-1100 in water. They contained 0.5% A-1100 solids on the surface. The band in *Figure 13* is an A-1100 filled interfilament channel running diagonally across the photograph. In *Figure 14* the channel is much wider and covers roughly the left hand side of this photograph. However, the glass surface areas appear to be at least as well covered as those of "E" glass having equivalent treatment. The flexural strength loss on boiling 12 hours in water for hoops made of this glass is 51%, magnitudes of loss greater than 8%, the loss of "E" glass hoops under the same conditions. Therefore, there must be something at the surface in this high modulus glass that is causing this drastic difference.

Continuously heat-cleaning G. E. continuous silica roving in oxygen-enriched air and finishing with a 1% solution of A-1100 in water is covered by data in *Table 4* and electron micrographs are given in *Figures 15* and *16*. Unfortunately, hoops were not made of this formulation. The available data shows that the coating of the A-1100 goes on this silica roving much the same as on "E" and high modulus glasses previously examined. The pick-up of solution, to give an initial 0.5% solids on the glass surface, is the same as the others, and a certain percentage (0.06% ± 0.02% in this sample or about two micromolecular layers in weight) is not removed by

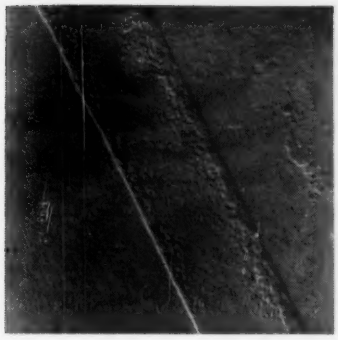


Figure 15.

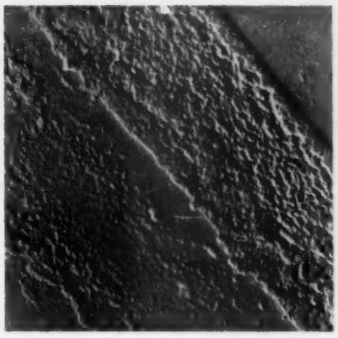


Figure 16.

Figure 15. 82,400X: The surfaces of two adjoining silica filaments with the inter-filament channel filled with amino alkyl siloxane. These filaments are a part of a silica roving that was continuously heat cleaned in oxygen enriched air and finished with a 1% solution of A-1100 in water

Figure 16. 82,400X: Another view of the sample presented in Figure 15

boiling. Since *all* three glasses appear to retain a residual of reacted A-1100 on their surface approximating one to two monolayers and, therefore, give evidence of the formation of a water-resistant bond to the glass in all three types, it is important to note that in the hoops the finish must transmit stress across this bond after the resin phase has absorbed water and therefore swelled, creating additional shearing stresses within the piece above those induced from outside forces. In the case of the "E" and G. E. silica glasses tested, the bonds, Si-O-Si, formed between coupling agent and glass were strong enough to remain essentially in force after the water adsorption of the composite on boiling. In the case of the beryllia-containing high modulus glass, it would appear that the reverse was true. It was explained in the above comparison of the Si-O-C bonds vs the Si-O-Si bonds that the former are more susceptible to strains introduced by resin swelling by water. When coated on a filament however, they are resistant to heat. In the high modulus glass some element is affecting the bonding strength of the silanols on the glass surface. The most likely candidate is this beryllia as mentioned above.

The Chrome Complex vs. Silane Coupling Agents

In Section IB of *Table 2*, Volan E, a chrome complex with an epoxy-reactive organic acid group (1), does not appear to bond at the interface to either the glass or this laminating resin with as strong a bonding as is obtained with an epoxy-reactive alkoxy silane. With Volan A, methacrylato chromic chloride, a strong or high stress resistant bonding has been found with this same (anhydride-epoxy) resin system (9). Others (1) have found in fabric laminates that Volan E appears to have high stress transfer bonding when used with an aromatic amine-hardened epoxy formulation, a better bonding in this case than that obtained using Volan A.

Please note that for the data presented in *Table 2* and in *Figure 7*, the formulation of the glass surface appears to be the deciding factor on the bond strength obtained from the coupling agent through to the glass, and that the differences run in about the same proportions but on a lower scale than for the silane. Repeating this work with Volan A would tend to give results approaching that obtained with A-1100 in the same anhydride-hardened epoxy bonding resin formulation.

Summary

The "silane" coupling agents can be strongly or weakly chemiadsorbed on relatively clean fiberglass surfaces. Whether the bond is of a high or low stress-transferring type, depends on whether it is affected by the swelling of the resin medium due to water adsorption during the immersion of a 70% by volume resin-bonded continuous glass filament hoop in boiling water.

In the three types of glass examined, the gamma amino propyl triethoxy silane (A-1100) coupling agent did form a bond to the glass by virtue of the fact that in each case a quantity amounting to the weight of 1-2 monolayers of amino propyl siloxane could not be removed by hot water from the surface of the glass, although an excess of this siloxane above this amount could be so removed.

In the case of "E" glass, it has been shown by others that epichlorohydrin will form, through the reaction of chlorine with the silanol groups, an Si-O-C bond that in an unstrained condition will not leave a glass surface up to a temperature of 350°C. Work presented here shows that this bond, from carbon through oxygen to the hydrolyzed silica structure of the glass, ruptures readily in hoops under the internally applied shearing stress of resin expansion due to moisture loading.

A very pure continuous filament silica roving can become sufficiently loaded with impurities of certain types of elements—the lighter alkali metals and those of the boron family (IIIb), to cause the surface to react much like that of "E" glass. Thus, in continuous filament winding, G.E.* continuous filament silica strand with these impurities may be expected to give results equivalent to "E" glass, if the quality of the individual filaments can be improved to allow tension loading per weight length of strand equal to "E" glass. Our work shows that the bonding from the laminating resin through the coupling agent to this silica glass is only about 6% less than that from the same resin and coupling agent to the "E" glass.

A comparison is made between the vapor phase treatment and various solution treatments of A-1100 on "E" glass which has been continuously heat-cleaned in oxygen-enriched air. Electron photomicrographs of

* General Electric Company

carbon-platinum shadowed replicates of these glass surfaces are introduced to show that the vapor phase treatment covers the glass much more completely than any solution method tried. It is this method of application that gave negligible loss of flexural strength properties of composites under 12 hour boil conditions for the "E" and silica glasses. Since this A-1100 vapor treatment of the beryllia-containing high modulus glass gave high loss of flexural strength of composites on boiling, and a micrograph of water applied A-1100 to the high modulus glass showed better than average surface coverage, it is not unreasonable to expect that the —Si—O—Si— bond between the coupling agent and the glass has some, but not sufficient, stress-carrying property to resist rupture when the resin in the composite swells in water.

It would also seem reasonable to believe that there is a connection between the poor surface bonding of the high modulus glass to the silane coupling agent and the break at pH 2.5-4.0 in an acid-base titration curve performed on the bare glass surface with dilute reagents. The cause of such a break in the curve would be the presence of a salt of a strong base and very weak acid. Alkali beryllium silicates in the formulation most likely would have such properties and could have a strong polarizing effect on neighboring silanol groups.

Another, but less effective, mechanism may be used to explain the apparent anomaly of the relatively excellent flexural strength retention properties of hoops made of A-1100 finished "E" glass strand, heat-cleaned as above, and the electron micrographs showing relatively poor covering of this glass surface by large, roughly-hemispherical agglomerates. Since it has been found that the polymerized amino alkyl siloxane will absorb but not dissolve in the anhydride-epoxy system used for laminating, and that since the normally water-soluble amino siloxane becomes relatively insoluble in the resin, it is suggested that the effect of this in-depth siloxane polymer cross-linked through the amino alkyl groups in depth to the epoxy resin gives more effective use of each reactive site on the glass and allows for bridging of non-reactive surface areas. This mechanism also can be used to explain the necessity shown by others (4) of applying the weight equivalent in water of eight monolayers (about 0.25%) loading on glass to obtain maximum properties in fabric laminates. The inter-filament channels will bridge and load and the surface must have a sufficiently large amino alkyl siloxane agglomerate per reactive area to absorb the shear loading in depth.

The organic acid group on the chrome complex coupling agent can be modified with various specific groups that appear to effect the reaction of the inorganic portion of the chrome complex with the epoxy resin used. The substituent group may or may not be epoxy-reactive to cause this effect. The action of the chrome complex with the glass surface is affected by the same changes in glass formulation as affected the silane coupling agent.

The interpretations of the data presented in this article are those of the author and are not to be construed as the opinion of his company, the associated companies, or that of the United States Government.

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A *preview* of several articles scheduled to appear in the next issue of SPE Transactions

The Relationship between the Structures of Organic Phosphites and their Effectiveness in Poly(Vinyl Chloride) Stabilization

by James P. Scullin, Marvin Rosen and Thomas A. Girard

Structural variation of an organic phosphite can markedly influence the color and heat stability of poly(vinyl chloride) in unfilled moderately plasticized systems containing barium and cadmium stabilizers. In this article which reports on the valuations of many structures, optimum activity was found with the alkyl-aryl phosphites.

Olefin Substituted Silicas as Active Fillers of Polymers

by I. E. Neimark, A. A. Chuiko and I. B. Sliniakova, especially translated for SPE TRANSACTIONS from Vyoskomolekularnye Soedineniya 3, 711-715 (1961)

Silicas in which the OH groups are substituted for organic radicals with double bonds are described. Incorporation of highly dispersed olefin substituted silica in methylmethacrylate during polymerization yields polymers with modified thermomechanical properties.

Novel Phosphorus Containing Polymers

by Lee M. Kindley, Harold E. Podall and Niclae Filipescu

Semi-organic polymers having metalloid atoms often improve flame resistance and thermal stability properties. Tris-hydromethyl phosphine oxide and its monobenzoylated derivative, both initially prepared from tetrakis hydromethyl phosphonium chloride, was used to study these effects with phosphorus containing polymers. Resultant properties are contrasted.

Radiation and Moisture Effects in Polymerized Epoxy Resins

by D. E. Kline and J. A. Sauer

The effects of moisture and large doses of reactor radiation on the dynamic properties of polymerized epoxy resins have been investigated over the temperature range 80° to 450°K and at frequencies from 200 to 1400 cps. Moisture absorption and irradiation cause shifts of the glass transition temperature. Irradiation also shifts the position of the damping peak. Explanations for these effects are given.

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THIS VITAL GROWING FIELD
WHEN YOU
COUNT ON TRANSACTIONS

SEE PREVIEWS FOR A LOOK
AT THE NEXT ISSUE.